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ANNUAL REPORTS  
ON THE  
PROGRESS OF CHEMISTRY.



# ANNUAL REPORTS

ON THE

## PROGRESS OF CHEMISTRY

### FOR 1927.

ISSUED BY THE CHEMICAL SOCIETY.

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# TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
<i>A.</i> . . . . .	Abstracts in Journal of the Chemical Society.
<i>A.</i> . . . . .	British Chemical Abstracts,* Section A.
<i>Acta Phytchim.</i> . . . . .	<i>Acta Phytchimica.</i>
<i>Acta Sci. Fennicae</i> . . . . .	<i>Acta Societatis Scientiarum Fennicae.</i>
<i>Amer. Chem. J.</i> . . . . .	American Chemical Journal.
<i>Amer. J. Bot.</i> . . . . .	American Journal of Botany.
<i>Amer. J. Pharm.</i> . . . . .	American Journal of Pharmacy.
<i>Amer. J. Physiol.</i> . . . . .	American Journal of Physiology.
<i>Amer. J. Sci.</i> . . . . .	American Journal of Science.
<i>Amer. Min.</i> . . . . .	American Mineralogist.
<i>Anal. Asoc. Quím. Argentina</i> . . . . .	Anales de la Asociación Química Argentina.
<i>Anal. Fis. Quím.</i> . . . . .	Anales de la Sociedad Española Física y Química.
<i>Analyst</i> . . . . .	The Analyst.
<i>Annalen</i> . . . . .	Justus Liebig's <i>Annalen der Chemie.</i>
<i>Ann. Acad. Sci. Fennicae</i> . . . . .	<i>Annales Academiae Scientiarum Fennicae.</i>
<i>Ann. Appl. Biol.</i> . . . . .	Annals of Applied Biology.
<i>Ann. Bot.</i> . . . . .	Annals of Botany.
<i>Ann. Chim.</i> . . . . .	<i>Annales de Chimie.</i>
<i>Ann. Chim. anal.</i> . . . . .	<i>Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.</i>
<i>Ann. Chim. Appl.</i> . . . . .	<i>Annali di Chimica Applicata.</i>
<i>Ann. Physik</i> . . . . .	<i>Annalen der Physik.</i>
<i>Ann. Physique</i> . . . . .	<i>Annales de Physique.</i>
<i>Ann. Reports</i> . . . . .	Annual Reports of the Chemical Society.
<i>Ann. Rep. Appl. Chem.</i> . . . . .	Annual Reports on the Progress of Applied Chemistry.
<i>Ann. Reports Roth. Exp. Sta.</i> . . . . .	Annual Reports of the Rothamsted Experimental Station.
<i>Ann. Sci. Univ. Jassy</i> . . . . .	<i>Annales scientifiques de l'Université de Jassy.</i>
<i>Ann. Soc. géol. Belg.</i> . . . . .	<i>Annales de la Société géologique de Belgique [including Mem. and Bull.], Liège.</i>
<i>Arch. exp. Path. Pharm.</i> . . . . .	<i>Archiv für experimentelle Pathologie und Pharmacologie.</i>
<i>Arch. Farm. sperim. Sci. aff.</i> . . . . .	<i>Archivio di Farmacologia sperimentale e Scienze affini.</i>
<i>Arch. Pharm.</i> . . . . .	<i>Archiv der Pharmazie.</i>
<i>Årsbok Sveriges Geol. Unders.</i> . . . . .	<i>Sveriges Geologiska Undersökning, Årsbok, Stockholm.</i>
<i>Atti R. Accad. Lincei</i> . . . . .	<i>Atti (Rendiconti, Memorie) della Reale Accademia Nazionale dei Lincei, classe di scienze fisiche, matematiche e naturali, Roma.</i>
<i>B.</i> . . . . .	British Chemical Abstracts,* Section B.
<i>Ber.</i> . . . . .	<i>Berichte der Deutschen Chemischen Gesellschaft.</i>
<i>Bied. Zentralbl.</i> . . . . .	<i>Biedermann's Zentralblatt.</i>
<i>Biochem. J.</i> . . . . .	The Biochemical Journal.
<i>Biochem. Z.</i> . . . . .	<i>Biochemische Zeitschrift.</i>

\* The year is not inserted in references to 1927.

# TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. vii

Abbreviated Title.	FULL TITLE.
<i>Biol. Zentralbl.</i> . . . .	Biologisches Zentralblatt.
<i>Bol. Acad. Nac. Ciencias, Córdoba</i> . . . . .	Boletín de la Academia Nacional des Ciencias, Córdoba.
<i>Bot. Gaz.</i> . . . . .	Botanical Gazette.
<i>Brit. Assoc. Reports</i> . . . .	Reports of the British Association for the Advancement of Science.
<i>Bul. Soc. chim. România</i> . . .	Buletinul Societății de Chimie din România.
<i>Bul. Soc. Româna Științe</i> . . .	Buletinul Societății Române de Științe.
<i>Bull. Acad. roy. Belg.</i> . . . .	Académie royale de Belgique—Bulletin de la Classe des Sciences.
<i>Bull. Chem. Soc. Japan</i> . . . .	Bulletin of the Chemical Society of Japan.
<i>Bull. int. Acad. Polonaise</i> . . .	Bulletin international de l'Académie Polonaise des Sciences.
<i>Bull. Soc. chim.</i> . . . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i> . . . .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. Chim. biol.</i> . . . .	Bulletin de la Société de Chimie biologique.
<i>Bull. Soc. franç. Min.</i> . . . .	Bulletin de la Société française de Minéralogie.
<i>Centr. Min.</i> . . . . .	Centralblatt für Mineralogie, Geologie und Paläontologie.
<i>Chem. and Ind.</i> . . . . .	Chemistry and Industry.
<i>Chem. Listy</i> . . . . .	Chemické Listy pro Vědu a Průmysl. Organ de la "Česká chemická Společnost pro Vědu a Průmysl."
<i>Chem. Met. Eng.</i> . . . . .	Chemical and Metallurgical Engineering.
<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Umschau</i> . . . . .	Chemische Umschau auf dem Gebiete der Fette, Öle, Wachse, und Harze.
<i>Chem. Weekblad</i> . . . . .	Chemisch Weekblad.
<i>Chem. Ztg.</i> . . . . .	Chemiker Zeitung.
<i>Cim.</i> . . . . .	Le Ciment.
<i>Compt. rend.</i> . . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Dcp. Agr. Union S. Afr. Sci. Bull.</i> . . . . .	Department of Agriculture, Union of South Africa, Scientific Bulletins.
<i>Deut. med. Wochenschr.</i> . . . .	Deutsche medizinische Wochenschrift.
<i>Engin. Mining J.</i> . . . . .	Engineering and Mining Journal.
<i>Fortschr. Landw.</i> . . . . .	Fortschritte der Landwirtschaft.
<i>Gazzetta</i> . . . . .	Gazzetta chimica italiana.
<i>Geol. För. Förh.</i> . . . . .	Geologiska Föreningens i Stockholm Förhandlingar.
<i>Giorn. Chim. Ind. Appl.</i> . . . .	Giornale di Chimica Industriale ed Applicata.
<i>Hawaii Exp. Sta. Bull.</i> . . . .	Hawaii Experimental Station Bulletins.
<i>Helv. Chim. Acta</i> . . . . .	Helvetica Chimica Acta.
<i>Ind. Eng. Chem.</i> . . . . .	Industrial and Engineering Chemistry.
<i>J.</i> . . . . .	Journal of the Chemical Society.
<i>Jahrb. Min. Beil.-Bd.</i> . . . .	Neues Jahrbuch für Mineralogie, Geologie, und Palaeontologie, Beilage-Band.
<i>Jahrb. wiss. Bot.</i> . . . . .	Jahrbuch für wissenschaftliche Botanik.
<i>J. Agric. Res.</i> . . . . .	Journal of Agricultural Research.
<i>J. Agric. Sci.</i> . . . . .	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Amer. Med. Assoc.</i> . . . . .	Journal of the American Medical Association.
<i>J. Amer. Pharm. Assoc.</i> . . . .	Journal of the American Pharmaceutical Association.
<i>J. Amer. Soc. Agron.</i> . . . . .	Journal of the American Society of Agronomy.
<i>J. Biol. Chem.</i> . . . . .	Journal of Biological Chemistry.
<i>J. Chem. Met. Soc. S. Africa</i> . . .	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
<i>J. Chim. phys.</i> . . . . .	Journal de Chimie physique.
<i>J. Exper. Med.</i> . . . . .	Journal of Experimental Medicine.
<i>J. Franklin Inst.</i> . . . . .	Journal of the Franklin Institute.
<i>J. Gen. Physiol.</i> . . . . .	Journal of General Physiology.
<i>J. Indian Chem. Soc.</i> . . . . .	Quarterly Journal of the Indian Chemical Society.



# viii TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

Abbreviated Title.	FULL TITLE.
<i>J. Indian Inst. Sci.</i> . . .	Journal of the Indian Institute of Science.
<i>J. Ind. Hygiene</i> . . .	Journal of Industrial Hygiene.
<i>J. Inst. Metals</i> . . .	Journal of the Institute of Metals.
<i>J. Ministry Agric.</i> . . .	Journal of the Ministry of Agriculture.
<i>J. Opt. Soc. Amer.</i> . . .	Journal of the Optical Society of America.
<i>J. Pharm. Belg.</i> . . .	Journal de Pharmacie de Belgique.
<i>J. Pharm. Exp. Ther.</i> . . .	Journal of Pharmacology and Experimental Therapeutics.
<i>J. Pharm. Soc. Japan</i> . . .	Journal of the Pharmaceutical Society of Japan. (Yakugakuzasshi.)
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. Pomology</i> . . .	Journal of Pomology and Horticultural Science.
<i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Roy. Micros. Soc.</i> . . .	Journal of the Royal Microscopical Society.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>J. Soc. Chem. Ind. Japan.</i> . . .	Journal of the Society of Chemical Industry, Japan. (Kōgyō Kwagaku Zasshi.)
<i>J. Soc. Chem. Japan</i> . . .	Journal of the Chemical Society of Japan. (Nippon Kwagaku Kwai Shi.)
<i>J. Soc. Dyers Col.</i> . . .	Journal of the Society of Dyers and Colourists.
<i>Kgl. Danske Vidensk. Selsk. math.-fys. Medd.</i> . . .	Kongelige Danske Videnskabsnens Selskab, matematisk-fysiske Meddelelser.
<i>Kgl. Landbruks Akad. Handl. Tid.</i> . . .	Kungliga Landbruks Akademiens Handlingar och Tidskrift.
<i>Klin. Woch.</i> . . .	Klinische Wochenschrift.
<i>Maryland Agr. Exp. Sta. Bull.</i> . . .	Maryland Agricultural Experimental Station Bulletins.
<i>Math.-Phys. Kl. Sächs. Akad.</i> . . .	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften (math.-phys. Klasse).
<i>Medd. K. Vetenskapsakad. Nobel-Inst.</i> . . .	Meddelanden från Kunglig-Vetenskapsakademiens Nobel-Institut.
<i>Mem. Manchester Phil. Soc.</i> . . .	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Mém. Soc. Russe Min.</i> . . .	Mémoires de la Société Russe de Minéralogie (Moscow and Leningrad).
<i>Mikrochem.</i> . . .	Mikrochemie.
<i>Min. Mag.</i> . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Mitt. deut. Landw.-Ges.</i> . . .	Mitteilungen der deutschen Landwirtschaft-Gesellschaft.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Nach. Ges. Wiss. Göttingen.</i> . . .	Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen.
<i>Naturwiss.</i> . . .	Die Naturwissenschaften.
<i>Natuurwetensch. Tijds.</i> . . .	Natuurwetenschappelijk Tijdschrift.
<i>Neue Jahrb. Min.</i> . . .	Neue Jahrbuch für Mineralogie.
<i>Norsk Geol. Tidsskrift</i> . . .	Norsk Geologisk Tidsskrift, Oslo.
<i>Notiz. chim.-ind.</i> . . .	Notiziario chimico-industriale.
<i>Off. Gazette Brit. Guiana.</i> . . .	Official Gazette, British Guiana, Georgetown.
<i>P.</i> . . .	Proceedings of the Chemical Society.
<i>Pharm. Weekblad</i> . . .	Pharmaceutisch Weekblad.
<i>Pharm. Zentr.</i> . . .	Pharmazeutische Zentralhalle.
<i>Pharm. Ztg.</i> . . .	Pharmazeutische Zeitung.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society of London.

# TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES. ix

Abbreviated Title.	FULL TITLE.
<i>Philippine J. Sci.</i> . . .	Philippine Journal of Science.
<i>Physical Rev.</i> . . .	Physical Review.
<i>Physikal. Z.</i> . . .	Physikalische Zeitschrift.
<i>Proc. Acad. Nat. Sci. Philadelphia</i> . . .	Proceedings of the Academy of Natural Sciences of Philadelphia.
<i>Proc. Amer. Acad. Arts Sci.</i> . . .	Proceedings of the American Academy of Arts and Sciences.
<i>Proc. Amer. Phil. Soc.</i> . . .	Proceedings of the American Philosophical Society.
<i>Proc. Amer. Soc. Hort. Sci.</i> . . .	Proceedings of the American Society of Horticultural Science.
<i>Proc. Camb. Phil. Soc.</i> . . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. Imp. Acad. Tokyo</i> . . .	Proceedings of the Imperial Academy of Japan.
<i>Proc. Indiana Acad. Sci.</i> . . .	Proceedings of the Indiana Academy of Sciences.
<i>Proc. K. Akad. Wetensch. Amsterdam</i> . . .	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Leeds Phil. Lit. Soc.</i> . . .	Proceedings of the Leeds Philosophical and Literary Society.
<i>Proc. Nat. Acad. Sci.</i> . . .	Proceedings of the National Academy of Sciences.
<i>Proc. Physical Soc.</i> . . .	Proceedings of the Physical Society of London.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Proc. Roy. Soc. New South Wales</i> . . .	Proceedings of the Royal Society of New South Wales.
<i>Rec. trav. chim.</i> . . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rend. Accad. Sci. fis. math. Napoli</i> . . .	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
<i>Rev. Mét.</i> . . .	Revue de Métallurgie.
<i>Sci. Papers Inst. Phys. Chem. Res. Tokyo</i> . . .	Scientific Papers of the Institute of Physical and Chemical Research, Tokyo.
<i>Sci. Proc. Roy. Dublin Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sci. Rep. Tôhoku Imp. Univ. Sitzungsber. Heidelberg. Akad. Wiss.</i> . . .	Science Reports, Tôhoku Imperial University. Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
<i>Sitzungsber. Preuss. Akad. Wiss. Berlin</i> . . .	Sitzungsberichte der Preussischen Akademie der Wissenschaften zu Berlin.
<i>Skrifter Norske Videnskaps-Akad.</i> . . .	Skrifter utgitt av det Norske Videnskaps-Akademi i Oslo. I, Matem.-Naturvid. Klasse.
<i>Soil Sci.</i> . . .	Soil Science.
<i>Trans. Amer. Electrochem. Soc.</i> . . .	Transactions of the American Electrochemical Society.
<i>Trans. Faraday Soc.</i> . . .	Transactions of the Faraday Society.
<i>Trans. oy. Soc. Canada</i> . . .	Transactions of the Royal Society of Canada.
<i>Ukraine Chem. J.</i> . . .	Ukrainian Chemical Journal.
<i>Univ. Calif. Pub. Agr. Sci.</i> . . .	University of California Publications in Agricultural Sciences.
<i>Univ. Toronto Studies, Geol. Ser.</i> . . .	University of Toronto Studies, Geological Series.
<i>U. S. Pub. Health Rep.</i> . . .	United States Public Health Reports.
<i>Ver. Ges. deut. Naturforsch. Aerzte</i> . . .	Verhandlungen der Gesellschaft deutscher Naturforscher und Aerzte.
<i>Videnskapsfel. Skrifter, Kristiania.</i> . . .	Videnskapsfel. Skrif. I. Mat.-naturv. Klasse, Kristiania.
<i>Wisconsin Agr. Exp. Sta. Res. Bull.</i> . . .	Wisconsin Agricultural Experimental Station Research Bulletins.
<i>Woch. Brau.</i> . . .	Wochenschrift für Brauerei.
<i>Z. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Z. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Z. anorg. Chem.</i> . . .	Zeitschrift für anorganische und allgemeine Chemie.
<i>Z. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Z. Krist.</i> . . .	Zeitschrift für Kristallographie.
<i>Z. Metallk.</i> . . .	Zeitschrift für Metallkunde.

# **X    TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.**

<i>Abbreviated Title.</i>	<i>FULL TITLE.</i>
<i>Z. Pflanz. Düng.</i> . . .	Zeitschrift für Pflanzenernährung und Düngung.
<i>Z. Physik</i> . . . . .	Zeitschrift für Physik.
<i>Z. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
<i>Z. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Z. Verein. deuts. Zuckerind.</i>	Zeitschrift des Vereins der deutschen Zucker- Industrie.

# ANNUAL REPORTS

## ON THE

### PROGRESS OF CHEMISTRY.

#### GENERAL AND PHYSICAL CHEMISTRY.

THE output of research in this branch of science continues to increase, and this fact is marked this year by the inclusion of a special Report on Chemical Kinetics (p. 314), a subject which includes two Meldola Medallists (1923 and 1926) amongst its workers in this country. No attempt has been made to report on the whole field of progress, and topics not recently dealt with have as far as possible been chosen for discussion.

#### *The Atomic Nucleus.*

Two papers of outstanding interest have been published this year, and it is considered that their importance justifies their inclusion here in anticipation of next year's Report on Radio-activity and Sub-atomic Phenomena.

The construction of an improved form of mass spectrograph has been described by F. W. Aston<sup>1</sup> in the Bakerian Lecture to the Royal Society. The new instrument has a resolving power five times, and an accuracy ten times, as great as the original one.<sup>2</sup> These improvements have been effected, not by a change of principle, but by doubling the angles of magnetic deflexion, and sharpening the lines by the use of finer slits placed farther apart. The dispersion varies from 1.5 mm. to 3 mm. for a change of mass of 1%, but owing to the fact that the lines on the plate are irregularly curved and change gradually in shape throughout the spectrum, it is necessary to compare masses, which must not differ by more than 1%, by the accurate measurement of (a) the distance between the lines, and (b) the dispersion constant at the mid-point between them. These measurements are applied in different ways to suit different cases, the most generally applicable one being a modification of the original bracketing method.

<sup>1</sup> *Proc. Roy. Soc.*, 1927, [A], **115**, 487; **A.**, 914.

<sup>2</sup> *Ann. Reports*, 1920, **17**, 221.

The results are now so accurate that the loss of an electron (mass = 0.00054;  $H = 1$ ) in the formation of a positive particle is generally significant and must be allowed for. Determinations of mass are now made to within 1—2 parts in 10,000 parts, and, as a result, it is found that most of the elements have atoms whose masses deviate from the whole-number rule, although not, of course, to the same extent as does hydrogen. In fact, there are now three fundamental numbers characteristic of every atom :

- (i) the *mass number*, giving the number of protons in the atom,
- (ii) the *atomic number*, giving the number of extranuclear electrons,
- (iii) the *packing fraction*, which is an indication of the forces binding the nuclear protons and electrons, and is thus a measure of the instability of the nucleus.

The packing fraction is 10,000 times the departure from the whole-number rule (when  $O = 16.000$ ) divided by the mass number, and has a value 77.8 for hydrogen. Since loss of mass may be taken as equivalent to release of energy due to close approach of protons and electrons in the nucleus and consequent partial annihilation of their electromagnetic fields, it follows that high packing fractions indicate looseness of packing and therefore low stability, and low packing fractions the reverse.

When the packing fractions of the atoms are plotted against their mass numbers, it is found that all but light atoms of even atomic number (helium, carbon, and oxygen) lie on a smooth, non-periodic curve which descends steeply from hydrogen (+ 77.8) through fluorine ( $\pm 0$ ) to a minimum at bromine ( $-9$ ), thereafter rising much more gently to cross the axis again at about mercury. The light atoms of even atomic number have packing fractions well below this curve, and approximate to a branch rising much less steeply to helium (+ 5.4). The observed stability of the nuclei of helium, carbon, and oxygen (beryllium has unfortunately not yet been measured) is in accord with their position on the lower curve.

Incidentally, the research has settled the isotopic constitutions of mercury and xenon, and has recorded new isotopes of sulphur and tin, bringing the number of isotopes of the last-named element up to eleven.

Sir E. Rutherford has put forward <sup>3</sup> a theory of the structure of the nucleus of a radioactive atom. The nucleus is imagined to consist of a central part around which revolve "neutrons"— $\alpha$ -particles plus two electrons (potential helium atoms)—in quant-

<sup>3</sup> *Phil. Mag.*, 1927, [vii], 4, 580; *A.*, 1002.

ised orbits. If the system should for some reason become unstable, the "neutron" is ejected as an  $\alpha$ -particle, and its two electrons circulate close to the central nucleus with a velocity approaching that of light. One of these may later be hurled from the atom as a  $\beta$ -ray. Either of these changes may be accompanied by a rearrangement of the "neutron" orbits involving the emission of  $\gamma$ -rays. In all cases the changes are governed by quantum relations.

*Refractivity and Refractive Dispersion.*

The departure from additivity of molecular refractivity has been calculated on the hypothesis that the electron shells of the atoms in the molecule are displaced (polarised) by the proximity of other atoms. The case for organic molecules is dealt with by K. Fajans and C. A. Knorr.<sup>4</sup> For saturated hydrocarbons the problem is simple. According to the Lewis-Langmuir electronic theory of valency, the 8 valency electrons of the carbon shell in methane are regarded as equally distributed amongst four carbon-hydrogen bonds, so that one-fourth of the molecular refraction of methane represents the value for one such bond. The refractive equivalent of a carbon-carbon linking may be obtained by subtracting six times the value of a carbon-hydrogen bond from the molecular refractivity of ethane. With substituted hydrocarbons, however, the problem is not so simple. Methyl chloride, for example, contains three carbon-hydrogen bonds and one carbon-chlorine linking, and the refractivity for the chlorine atom in these circumstances is considered to be due to the combined influence of the bonding pair of electrons and the three lone pairs. It is thus nearly the same as the refractivity of the chlorine atom in hydrogen chloride and is lower than the refractivity for the free chlorine ion. The refractivities for a large number of groupings are worked out in this way. Somewhat similar considerations are applied by T. H. Havelock,<sup>5</sup> who treats atoms as isotropic resonators in fixed relative positions in the molecule.

The case for ions in solution has been worked out by K. Fajans,<sup>6</sup> who points out that the refractivity of an ion is a measure of the ease of displacement of its electron shells with respect to the nucleus. An anion is rendered more rigid by the proximity of positively charged kations, since the positive charges tend to balance the inward attraction of the positively charged nucleus. Its refractivity thus tends to fall. Conversely, the proximity of negatively charged anions tends to displace the electron shells of a

<sup>4</sup> *Ber.*, 1926, 59, [B], 249; *A.*, 1926, 336.

<sup>5</sup> *Phil. Mag.*, 1927, [vii], 3, 158, 433; *A.*, 189, 294.

<sup>6</sup> *Trans. Faraday Soc.*, 1927, 23, 357; *A.*, 1023.

kation, since now the attractive force of the nucleus is reinforced by the repulsive effect of the neighbouring anions. Its refractivity therefore tends to rise. "The union of ions into molecules or crystals will thus be accompanied by a net diminution of the refractivity whenever the consolidating effect of the kation upon the anion outweighs the loosening effect of the anion on the kation, and *vice versa*."

K. F. Herzfeld and K. L. Wolf <sup>7</sup> and B. Davis <sup>8</sup> have attempted to fit dispersion equations involving one or more frequency terms to the observed data for elements and compounds, but R. A. Morton and R. W. Riding consider <sup>9</sup> that no satisfactory two-term equation for the variation of refractive index with wave-length can be obtained until further absorption data are secured in the short-wave ultra-violet region of the spectrum. They are of the opinion that existing data are best fitted by equations of the type : <sup>10</sup>

$$(n - 1)(V_1 + V_2 + V_3 + \dots) = V_1 N_1 / (v_1^2 - v^2) + V_2 N_2 / (v_2^2 - v^2) + V_3 N_3 / (v_3^2 - v^2) + \dots$$

where  $n$  represents the refractive index;  $V_1, V_2$ , etc., the volumes of the respective molecular phases; <sup>11</sup>  $N_1, N_2$ , etc., constants associated with the respective molecular phases;  $v$  the frequency at which the refractive index is observed; and  $v_1, v_2$ , etc., the oscillation frequencies associated with the respective molecular phases and are all integral multiples of a fundamental frequency in the infra-red.

The conclusions of H. Hunter <sup>12</sup> and others <sup>13</sup> that the neglect of the dispersion factor is possibly responsible for the failure of the generally accepted methods of applying refractometric data to problems of chemical constitution receive experimental support from the work of H. Voellmy.<sup>14</sup> This author has examined the molecular refractivities of more than 30 organic liquids at wave-lengths between 6560 and 2100 Å., and has shown that the refractivity does, in fact, increase on the long wave-length side of an absorption band and decrease on the other side in accordance with theory.

Workers on refractivity in the infra-red will do well to note the warning of Sir R. Robertson and J. J. Fox,<sup>15</sup> that the temperature

<sup>7</sup> *Ann. Physik*, 1925, [iv], **76**, 71; *A.*, 1925, ii, 182.

<sup>8</sup> *Physical Rev.*, 1925, [iii], **26**, 232; *A.*, 1925, ii, 933.

<sup>9</sup> *Phil. Mag.*, 1926, [vii], **1**, 726; *A.*, 1926, 558.

<sup>10</sup> E. C. C. Baly and R. A. Morton, *J. Physical Chem.*, 1924, **28**, 659; *A.*, 1924, ii, 714.

<sup>11</sup> *Ann. Reports*, 1915, **12**, 6.

<sup>12</sup> *Ibid.*, 1923, **20**, 15.

<sup>13</sup> F. R. Goss, C. K. Ingold, and J. F. Thorpe, *J.*, 1924, **125**, 1927.

<sup>14</sup> *Z. physikal. Chem.*, 1927, **127**, 305; *A.*, 812.

<sup>15</sup> *Nature*, 1927, **119**, 818; *A.*, 607.

coefficients of refractive index for rock salt and fluorite are important and cannot be neglected.

*Molecular Volume.*

One of the outstanding achievements of the electronic theory of valency is the prediction of two kinds of double bond—the semi-polar double bond, occurring mainly but not exclusively in inorganic compounds, and the non-polar double bond which is chiefly, but again not entirely, to be found in carbon compounds. For some time after the theoretical prediction of the existence of the semi-polar double bond there was no experimental method of detecting its presence; now, however, there are three methods available. In order of priority we have : (a) the parachor,<sup>16</sup> (b) resolution into optical enantiomorphs,<sup>17</sup> (c) zero volume.<sup>18</sup>

Of these, (b) is an absolute method, but is obviously limited in application to a very few compounds, although it can be applied to solids as well as to liquids, (a) is of more extended applicability, but is limited to non-associated liquids, whilst (c) can be applied to all liquids.

Method (b) is outside the scope of this Report. The principle underlying method (a) has already been described,<sup>19</sup> but has recently been greatly extended in application. The examination<sup>20</sup> of a large number of double-bonded compounds by the method of the parachor has shown that such substances fall into two sharply defined classes, one showing an increase in the parachor of 23.2 units due to the presence of the double bond, and the other a decrease of 1.6 units. The evidence is clear that the first class represents the non-polar linking and the second the semipolar. It is found that in every case where a carbon atom is concerned in the double bond the linking is non-polar. T. M. Lowry's suggestion to the contrary,<sup>21</sup> improbable enough on other grounds, is thus ruled out of court, at all events as far as molecules not in a reacting state are concerned.

A later paper<sup>22</sup> lends support to the view that the double bonds in maleic-fumaroid geometrical isomerides are non-polar, and indicates that isomerism of this type has little or no effect on the

<sup>16</sup> S. Sugden, *J.*, 1924, **125**, 1185.

<sup>17</sup> H. Phillips, *J.*, 1925, **127**, 2552; P. W. B. Harrison, J. Kenyon, and H. Phillips, *J.*, 1926, 2079; S. G. Clarke, J. Kenyon, and H. Phillips, *J.*, 1927, 188.

<sup>18</sup> S. Sugden, *J.*, 1927, 131.

<sup>19</sup> *Ann. Reports*, 1924, **21**, 8.

<sup>20</sup> S. Sugden, J. B. Reed, and H. Wilkins, *J.*, 1925, **127**, 1525.

<sup>21</sup> *J.*, 1923, **123**, 822.

<sup>22</sup> S. Sugden and H. Whittaker, *J.*, 1925, **127**, 1525.



parachor. A similar conclusion,<sup>23</sup> that *o*-, *m*-, and *p*-isomerides have identical values for the parachor, has also been reached. The evidence of the parachor in every case supports the maintenance of the octet as against shells of 6, 10, or 12 electrons. S. Sugden and H. Wilkins have determined the effect of ring structure on the parachor,<sup>24</sup> and have correlated the values so found with the degree of unsaturation measured as the quotient of the number of latent valencies by the number of octets involved. The figures, given below, are striking.

Structure.	Latent valencies ( <i>x</i> ).	Octets ( <i>n</i> ).	Degree of unsatur- ation ( <i>x/n</i> ).	Parachor,	
				obs.	calc.
Triple bond .....	4	2	2.000	46.6	46.4
Double bond .....	2	2	1.000	(23.2)	(23.2)
Three-membered ring .....	2	3	0.667	17	15.5
Four-membered ring .....	2	4	0.500	11.6	11.6
Five-membered ring .....	2	5	0.400	8.5	9.3
Six-membered ring .....	2	6	0.333	6.1	7.7

The view that structural constants affecting the parachor have values proportional (to a first approximation) to the degree of unsaturation involved receives additional support from the value found for the semipolar double bond (−1.6); this bond is not unsaturated and therefore we should expect it to have no influence on the parachor. The slight negative value actually observed is probably due to a small contraction in volume caused by electrostatic attraction (rendered obvious when the semipolar double bond is written thus :  $\overset{+}{\text{S}}-\overset{-}{\text{O}}$ ).

Compounds of phosphorus and arsenic have been examined,<sup>25</sup> and Sugden considers that the formula suggested by E. B. R. Prideaux<sup>26</sup> for phosphorus pentachloride, which involves a single-electron bond ("singlet") between the phosphorus atom and each of two of the chlorine atoms linked to it, the other three being held in the normal manner by duplets, best represents the facts. This has the advantage that it preserves the rule of eight inviolate, but N. V. Sidgwick<sup>27</sup> considers another explanation preferable. Finally, F. B. Garner and S. Sugden<sup>28</sup> have applied the method to decide between tautomeric ring and chain formulæ for quinones, benzils, and succinyl and phthalyl chlorides, and find that all except the last-named have the normal structure and cannot in the liquid form contain more than traces of the ring isomeride. In

<sup>23</sup> S. Sugden and H. Wilkins, *J.*, 1927, p. 2517.

<sup>24</sup> *Idem, ibid.*, 1927, 139.

<sup>25</sup> *Ibid.*, p. 1174.

<sup>26</sup> *Chem. and Ind.*, 1923, 42, 672.

<sup>27</sup> "The Electronic Theory of Valency," Oxford Univ. Press, 1927, p. 130.

<sup>28</sup> F. B. Garner and S. Sugden, *J.*, 1927, 2877.

the case of phthalyl chloride, the high-melting form was shown to have the unsymmetrical, and the low-melting form the symmetrical, structure.

Sugden has also shown<sup>29</sup> that the variation of density with temperature from the freezing point to the critical point is represented accurately for normal liquids by the equation :

$$D - d = D_0(1 - T/T_c)^{0.3},$$

where  $D$  and  $d$  are the densities of the liquid and vapour at  $T^\circ \text{K.}$ ,  $T_c$  is the critical temperature on the same scale, and  $D_0$  is a constant representing the liquid density at absolute zero. This equation also holds for associated liquids at lower temperatures. The "zero volume,"  $V_0$ , obtained by dividing the molecular weight by  $D_0$ , is found to be nearly proportional to the critical volume, the factor of proportionality being about 0.27.

The zero volume thus obtained is an additive function of the following constants,<sup>30</sup> the observed values lying within 2% of those calculated for 236 out of 284 compounds considered.

Atomic constants.			Structural constants.	
H = 6.7	I	= 28.3	Triple bond	= 15.5
C = 1.1	P	= 12.7	Double bond	= 8.0
N = 3.6	S	= 14.3	Three-membered ring	= 4.8
O = 5.0	O (in alcohols)	= 3.0	Four-membered ring	= 3.2
F = 10.3	N (in amines)	= 0.0	Five-membered ring	= 1.8
Cl = 19.3			Six-membered ring	= 0.6
Br = 22.1			Sempolar double bond	= 0.0

The difference between the values for non-polar and semipolar double bonds is noteworthy, and it will be observed that there is the same connexion between the values for the structural constants and their degree of unsaturation as in the case of the parachor, although the quantitative agreement is not so good.

Other, less successful, relationships<sup>31</sup> have been put forward recently, notably  $V_0 p_c / T_c = \text{const.}$  and modifications of this ( $p_c$  here represents the critical pressure, the other symbols have their previous significance). W. Herz<sup>32</sup> has also correlated  $V_0$  with latent heat of vaporisation, the Poisson capillarity constant, molecular elevation of the boiling point, and the difference between the specific heats at constant pressure and constant volume. A close connexion between molecular volume and molecular refractivity,<sup>33</sup>

<sup>29</sup> F. B. Garner and S. Sugden, *J.*, 1927, 1780.

<sup>30</sup> *Ibid.*, p. 1786.

<sup>31</sup> R. Lorentz and W. Herz, *Z. anorg. Chem.*, 1924, **140**, 379; 1925, **141**, 375; *A.*, 1925, ii, 25, 183; W. Herz, *ibid.*, 1925, **149**, 270; 1926, **153**, 339; *A.*, 1926, 110, 778.

<sup>32</sup> *Ibid.*, 1926, **153**, 269; *A.*, 1926, 786.

<sup>33</sup> R. Lorentz and W. Herz, *ibid.*, 1925, **142**, 80; *A.*, 1925, ii, 356.

and between molecular refractivity and the parachor<sup>34</sup> have also been indicated.

*The Metastability of Matter.*

The view that elements and compounds, even when chemically pure, may not be physically homogeneous, is gradually gaining ground and seems destined to prove of great importance. Only a few years ago, the phenomena of allotropy and polymorphism were regarded as the exception rather than the rule, yet to-day E. Cohen<sup>35</sup> is able to state his belief that "every solid substance may exist in two or more modifications" and that "many of the hitherto recognised physical or physicochemical constants of solid substances are values which refer very often, if not always, to metastable mixtures which contain two or more modifications of that substance in unknown proportions" so that "no definite importance can be assigned to such constants." This behaviour of solids—their disinclination to change at once into stable modifications at the appropriate transition point—is, of course, not an unmixed evil. Many of the special steels, to take a familiar example, depend for their properties on constituents deliberately added to prevent such change. Nevertheless, such wholesale doubt cast upon the accuracy of physical properties, determined without special precautions to ensure physical as well as chemical purity, is disturbing. Nor is the doubt confined to solids. Liquids and gases—as shown by experiments on intensive drying—must also be considered, even when chemically pure, as more or less complex mixtures.

In the case of some substances, of course, it has long been known that metastability over a long period of time occurs. E. Cohen<sup>36</sup> has recently directed attention to the fact that as long ago as 1847, St. Claire Deville pointed out that the stabilisation of solid sulphur at the ordinary temperature was not complete even after 8 years, as indicated by a progressive change in density. In the classical case of tin, too, it has been shown that the physical properties are dependent on the previous thermal history of the sample,<sup>37</sup> and it is only recently<sup>38</sup> that the true densities and specific heats of the white and grey varieties have been determined. A similar uncertainty exists in the case of lead.<sup>39</sup>

<sup>34</sup> W. Herz, *Z. anorg. Chem.*, 1927, **159**, 316; *A.*, 189.

<sup>35</sup> "Physico-chemical Metamorphosis and Problems in Piezo-chemistry," McGraw-Hill, 1926, p. 50.

<sup>36</sup> *Z. physikal. Chem.*, 1924, **109**, 109; *A.*, 1924, ii, 450. See also "The Phase Rule," A. Findlay, Longmans, 1923.

<sup>37</sup> A. Travers and Huot, *Compt. rend.*, 1927, **184**, 152; *A.*, 194.

<sup>38</sup> E. Cohen and K. D. Dekker, *Z. physikal. Chem.*, 1927, **127**, 183; *A.*, 818.

<sup>39</sup> D. Cannegieter, *Chem. Weekblad*, 1927, **24**, 350; *A.*, 818.

Compounds are equally difficult to deal with. The different crystal structures—cubic and hexagonal—assigned to silver iodide by different workers are considered<sup>40</sup> to be due to the metastable existence of one form in the stable region of the other. The heats of solution of two forms of cadmium iodide have been measured<sup>41</sup> and earlier discrepant results shown to be due to physical heterogeneity. Ammonium nitrate is a particularly glaring case investigated by R. G. Early and T. M. Lowry.<sup>42</sup> It can exist in no fewer than six solid modifications, and recent determinations of the transition temperature of, and the volume change accompanying, the  $\text{III} \rightleftharpoons \text{IV}$  transformation have been made,<sup>43</sup> confirming the temperature found by Lowry and Early, but differing by 8% from the volume change determined by Bridgman.<sup>44</sup>

The question of the preparation of physically pure modifications of a substance is a difficult one. Since, in any change of state, metastable modifications may be produced in preference to stable ones (Ostwald's rule of the succession of phases) it is obvious that crystallisation, freezing, sublimation, distillation, etc.—the very methods employed for *chemical* purification—will almost inevitably lead to the formation of metastable modifications. The question of physical purification therefore resolves itself into one of accelerating the stabilising change after the metastable modification has been produced, and it has been shown that repetition of the transition process a number of times is one method of effecting this<sup>45</sup>—the presence of a solvent for one form,<sup>46</sup> or even of water<sup>47</sup> or electrolytes, is another. The presence of adsorbed impurities<sup>48</sup> is also effective in many cases. The only evidence of physical purity is the constancy of physical properties of different specimens—a negative test, but the only one available.

The effect of intensive drying on the properties of liquids and solids has been studied—particularly by H. B. Baker,<sup>49</sup> A. Smits,<sup>50</sup> and S. B. Mali.<sup>51</sup> The results obtained by Smits on the self-

<sup>40</sup> E. Cohen and A. L. T. Moesveld, *Z. physikal. Chem.*, 1924, **109**, 97; *A.*, 1924, ii, 450.

<sup>41</sup> E. Cohen, W. D. Helderman, and A. L. T. Moesveld, *ibid.*, p. 100; *A.*, 1924, ii, 450.

<sup>42</sup> *J.*, 1919, **115**, 1387.

<sup>43</sup> E. Cohen and J. Kooy, *Z. physikal. Chem.*, 1924, **109**, 81; *A.*, 1924, ii, 449.

<sup>44</sup> *Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581.

<sup>45</sup> "Physico-chemical Metamorphosis, etc.," p. 87.

<sup>46</sup> E. Cohen and A. L. T. Moesveld, *Z. physikal. Chem.*, 1920, **94**, 450; *A.*, 1920, ii, 611.

<sup>47</sup> *Vide infra*, Ref. 58.

<sup>48</sup> *Amer. J. Sci.*, 1916, [iv], **16**, 504.

<sup>49</sup> *Inter alia*, *J.*, 1922, **121**, 568.

<sup>50</sup> *Inter alia*, *J.*, 1924, **125**, 2573.

<sup>51</sup> *Z. anorg. Chem.*, 1925, **149**, 150; *A.*, 1926, 117.

intensive drying of sulphur trioxide and phosphorus pentoxide have already been described.<sup>52</sup> The general effect of intensive drying on liquids has been to lower the vapour pressure, but that of nitrogen tetroxide<sup>53</sup> was raised. H. B. Baker has now shown that changes in vapour pressure and molecular complexity in liquids can be produced by means of catalysts (the author's term) such as charcoal, platinum-black, or thoria.<sup>54</sup> His view is that "all liquids may be regarded as analogous to a dissociable gas such as nitrogen tetroxide. . . . Liquids differ, however, in this respect, that dissociation and association are much slower in liquids than in gases. Equilibrium in liquids may be profoundly disturbed by even a comparatively slight change of temperature, and complete recovery of the normal condition may be a question of weeks or even months." These observations are confirmed by J. B. Peel, P. L. Robinson, and H. C. Smith,<sup>55</sup> who report changes in density under similar conditions. The following figures for water with thoria as catalyst give an idea of the magnitudes of the observed changes :

Molecular complexity.		Density.	
After 3 weeks	3.125 $\times$ 18	After 1 day	- 0.00017
5 weeks	3.612 $\times$ 18	2 days	-- 0.00002
9 weeks	3.866 $\times$ 18	4 days	+ 0.00001
		8 days	+ 0.00011
		9 days	+ 0.00015

Vapour pressure : + 2.4 mm. before heating; + 4.0 mm. after heating at 80° for 48 hrs., then cooling to 20°; + 1.2 mm. 1 day later; + 0.9 mm. 2 weeks later.

In this connexion, the observations of G. Tammann<sup>56</sup> are of interest. This author, from an examination of specific volume and compressibility data, deduces the presence of large molecules of "water-I," (H<sub>2</sub>O)<sub>6</sub>, with the space lattice of ice-I. The concentration of these molecules falls with rise of temperature or pressure, and disappears at 50° or 2500 kg./cm.<sup>2</sup>. With regard to the effect of intensive drying on the properties of liquids, D. Balarev<sup>57</sup> states that repetition of Baker's experiments gave liquids which invariably contained phosphorus, and he suggests that the formation of volatile compounds of phosphorus is the cause of the observed phenomena. Baker, however, has pointed out<sup>57a</sup> that, apart from the fact that the large elevations of boiling point observed could not be due to this cause, his published paper definitely states that all the

<sup>52</sup> *Ann. Reports*, 1924, 21, 30.

<sup>53</sup> A. Smits, W. de Liefde, E. Swart, and A. Claassen, *J.*, 1926, 2657; J. W. Smith, *J.*, 1927, 867.

<sup>54</sup> *J.*, 1927, 949.

<sup>55</sup> *Nature*, 1927, 120, 514; *A.*, 1019.

<sup>56</sup> *Z. anorg. Chem.*, 1926, 158, 1; *A.*, 1927, 93.

<sup>57</sup> *J. pr. Chem.*, 1927, [ii], 116, 57; *A.*, 613.

<sup>57a</sup> *J.*, 1927, 2902.

liquids were examined for phosphorus, with negative results. He suggests that Balarev's results are possibly due to the presence of volatile phosphorus trioxide in the pentoxide used.

A. Smits<sup>58</sup> considers that every phase of an allotropic substance contains different molecular species which may be isomerides, polymerides, or dissociation products of the simple molecule. Normally, inner equilibrium between these forms is rapidly established, and the system behaves as a unary one, but in certain circumstances (intensive drying) the establishment of this inner equilibrium may be rendered very slow, or even stopped altogether. Alternatively, the inner equilibrium may be first displaced and then fixed in its new position. In the simple case where two components only are concerned, three cases may arise :

FIG. 1.

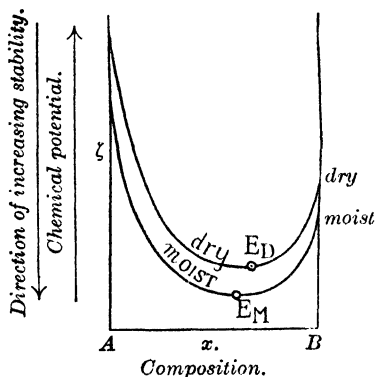
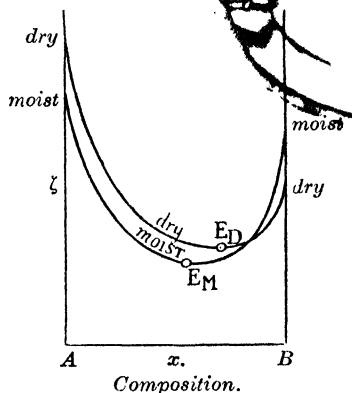


FIG. 2.



(i) Both forms are more stable in the moist than in the dry state. Then two curves for the chemical potential ( $\zeta$ ) as a function of the composition ( $x$ ) are obtained (Fig. 1), and it will be a coincidence if both curves have minima (equilibrium points) at identical values of  $x$ . The equilibrium position will therefore be shifted by intensive drying, but the direction of the change cannot be predicted.

(ii)  $A$  may be more stable in the moist, and  $B$  in the dry, state. We then get the condition of affairs represented in Fig. 2 and the conclusions are as before.

(iii) Intensive drying may have no effect on the stability of either form—the  $\zeta$ - $x$  curves for moist and dry conditions are then identical, and no effect will be produced by intensive drying.

It is obvious that these views can be applied to the action of catalysts other than water.

<sup>58</sup> *J.*, 1926, 2655. Compare A. Smits, "The Theory of Allotropy," Longmans, 1922.

*Strong Electrolytes.*

The Debye-Hückel theory still continues to attract considerable attention and much work has appeared on this subject during the year. Hence, although this section was included in the Reports for the last two years, which stressed mainly the agreement of the theory with observation, the opportunity is taken this year of recording some of the work which has gone to make up the other side of the picture.

W. D. Bancroft<sup>59</sup> has revived H. E. Armstrong's conception of the complexity of water, although in a more comprehensible form. He suggests that many of the anomalies of strong electrolytes, in particular the neutral-salt effect and the failure of the Ostwald dilution law, may be due to a disturbance of the equilibria between the various polymerised or associated molecules of which liquid water is generally considered to consist. He is of the opinion that "there is very little to be gained by devising empirical formulas which ignore this factor." His pronouncement,<sup>60</sup> that physical chemists in this field are ignoring reality and working with "slightly polluted water," since their formulæ break down at concentrations greater than about 0.01*M*, will possibly pass into history.

The bulk of the work recorded goes to demonstrate the essential correctness of the theory and, where disagreement is expressed, it is generally on matters of detail. On the question of complete ionisation, for instance, the Arrhenius theory leads to figures for uni-univalent strong electrolytes from conductivity measurements of about 90—95% ionisation at about 0.01—0.001*M*, whereas the new theory demands 100%. The tendency now seems to be to admit a compromise, in some cases up to a figure of 3% (or thereabouts) of ionic association. For instance, K. Fajans<sup>61</sup> has employed refractometric means to test the theory and finds that his measurements indicate, in general, incomplete ionisation and, in particular, that in solution a chlorine ion can approach more closely to a lithium ion than to a sodium ion, a conclusion in direct conflict with the theory. It is urged, therefore, that the parameter which Debye calls the radius of the ionic atmosphere has not really that physical significance. D. A. MacInnes and I. A. Cowperthwaite,<sup>62</sup> from measurements of transport numbers, draw similar conclusions. L. Onsager<sup>63</sup> has modified the Debye-Hückel equation for conductivity<sup>64</sup>

$$\Lambda_0 - \Lambda_c = \Lambda_0(K_1 w_1 + K_2 b) \sqrt{2c}$$

<sup>59</sup> *J. Physical Chem.*, 1926, **30**, 1184.

<sup>60</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 94 (Jubilee No.).

<sup>61</sup> This Report, p. 13.      <sup>62</sup> *Trans. Faraday Soc.*, 1927, **23**, 400; **A.**, 1031.

<sup>63</sup> *Ibid.*, p. 341; **A.**, 1031.

<sup>64</sup> *Ann. Reports*, 1925, **22**, 36.

by introducing a correction for the Brownian movement of the ions. In the case where the mobilities of the ions of a uni-univalent electrolyte are equal, the correction term becomes  $2 - \sqrt{2}$ , so that the equation becomes

$$\Lambda_0 - \Lambda_c = \Lambda_0[K_1(2 - \sqrt{2}) + K_2b]\sqrt{2c}$$

since  $w_1 = \frac{1}{2}(l_a/l_c + l_c/l_a)$ , where  $l_a$  and  $l_c$  are the mobilities and are equal in this case. For potassium chloride, with  $\Lambda_0 = 129.9$ , the original expression leads to

$$\Lambda_0 - \Lambda_c = 0.547\sqrt{2c},$$

whereas Onsager's gives

$$\Lambda_0 - \Lambda_c = 0.433\sqrt{2c},$$

as against the experimentally observed value  $0.461\sqrt{2c}$ . Even then, however, the results indicate association of the ions into molecules at quite low concentrations. H. B. Hartley and R. P. Bell,<sup>65</sup> from conductivity data, and C. A. Kraus and R. P. Seward,<sup>66</sup> from solubility data, consider that incomplete ionisation must be recognised in solvents other than water and possibly methyl alcohol. Both G. Nonhebel,<sup>67</sup> from *E.M.F.* measurements, and C. W. Davies,<sup>68</sup> from conductivity measurements, prefer the Milner coefficient in the activity equation

$$\log f = -A\sqrt{c}$$

to express their results. (For uni-univalent electrolytes, the Debye-Hückel theory requires  $A = 0.5$ , and the Milner theory at significant concentrations requires  $A =$  about 0.39.)

The failure of the Debye-Hückel theory to deal with the case of small ions of high valency has been shown by N. Bjerrum<sup>69</sup> and D. L. Chapman<sup>70</sup> to be due to the inapplicability of the approximation  $\sinh \epsilon\psi/kt = \epsilon\psi/kt$  under these conditions. W. Nernst and W. Orthmann<sup>71</sup> state that the heats of dilution of salts of the same valency type at low and very low concentrations are not the same, and are in some cases even negative, and hence do not agree with the theory, and their view receives partial support from the work of P. Grosz.<sup>72</sup> N. Bjerrum,<sup>73</sup> however, asserts that these and

<sup>65</sup> *Trans. Faraday Soc.*, 1927, **23**, 396; **A.**, 1032.

<sup>66</sup> *Ibid.*, p. 488; **A.**, 1021.

<sup>67</sup> *Phil. Mag.*, 1926, [vii], **2**, 1085; **A.**, 1927, 21.

<sup>68</sup> *Ibid.*, 1927, [vii], **4**, 244; **A.**, 936.

<sup>69</sup> *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1926, **7**, [9], 1; **A.**, 1927, 314.

<sup>70</sup> *Trans. Faraday Soc.*, 1927, **23**, 443.

<sup>71</sup> *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1926, 51; 1927, 136; **A.**, 1926, 579; 1927, 733.

<sup>72</sup> *Monatsh.*, 1927, **48**, 243; **A.**, 940.

<sup>73</sup> *Trans. Faraday Soc.*, 1927, **23**, 445; **A.**, 1028.



other small discrepancies may be quantitatively explained by assuming a decrease of the effective dielectric constant of the solution in the immediate neighbourhood of the ions.

One clear-cut issue is the formulation of an equation to represent the conductivity of a strong electrolyte as a function of the concentration. Four such equations have recently been proposed :

$$(1)^{74} \quad 1 - \Lambda_c/\Lambda_0 = 0.5(\nu - 1)[\beta c^{0.5} - 2\gamma c + 3\delta c^{1.5} \dots]$$

$$(2)^{75} \quad \Lambda_0 - \Lambda_c = Bc^n$$

$$(3)^{76} \quad \Lambda_0 - \Lambda_c = Ac^{0.5} - ABc$$

$$(4)^{77} \quad \Lambda_0 - \Lambda_c = A/(B + c^{0.5})$$

where  $\Lambda_0$  and  $\Lambda_c$  are the equivalent conductivities at infinite dilution and concentration  $c$ , respectively,  $\nu$  is the number of ions into which the electrolyte dissociates, and  $\beta$ ,  $\gamma$ ,  $\delta$ ,  $A$ ,  $B$ , and  $n$  are constants typical of the electrolyte. Of these, all except (2) are devised to reduce to the form

$$\Lambda_0 - \Lambda_c = Xc^{0.5}$$

when  $c$  is small, in order to be so far in accord with the Debye-Hückel theory. Equation (2) has the advantage that it does not prejudice the issue as to the value for the index for  $c$ . By suitable choice of variables, Ferguson and Vogel have established the facts, not only that equation (2) will represent the experimental figures, but also that  $n$ , *when determined without any preconceived ideas as to its value*, never has the value 0.5, and varies from electrolyte to electrolyte. Their view is that  $n$  and  $B$  are functions of the ionic masses and that conductivity measurements do not support the Debye-Hückel theory, at least in its present form. Their conclusions are that

(a) the constants  $B$  and  $n$  vary from electrolyte to electrolyte in a regular manner for related electrolytes ;

(b) the extreme variations of  $n$  are from 0.3742 for potassium chloride at 25° to 0.9687 for iodic acid at the same temperature, although most of the values lie within 20% of 0.5 ;

(c) both  $B$  and  $n$  vary with temperature, although there are not sufficient data available to determine the precise mode of this variation ;

(d) the formula is applicable to uni-uni-, uni-bi-, and bi-bi-valent electrolytes, and to water and (as far as data are available) methyl

<sup>74</sup> B. Szyzskowski, *Bull. Acad. Polonaise*, 1926, [A], 325; *A.*, 1927, 415.

<sup>75</sup> A. Ferguson and I. Vogel, *Phil. Mag.*, 1925, [vi], 50, 971; 1927, [vii], 4, 1, 233, 300; *Trans. Faraday Soc.*, 1927, 23, 404; *A.*, 1925, ii, 1163; *A.*, 1936, 941; I. Vogel, *Phil. Mag.*, 1928, [vii], 5, 199.

<sup>76</sup> *Inter alios*, L. Onsager, *Trans. Faraday Soc.*, 1927, 23, 341.

<sup>77</sup> R. T. Lattey, *Phil. Mag.*, 1927, [vii], 4, 831.

alcohol and nitromethane as solvents. It is also applicable to strong acids such as hydrochloric and iodic.

It is of course possible that their results are capable of other interpretations. The fact that an empirical equation will fit given sets of figures is no guarantee at all that it is the correct equation to apply, and it is obvious that the good agreement obtained by Ferguson and Vogel by variation of the coefficient and the exponent of  $c$  can equally well be obtained by varying  $A$  and  $B$  in equations (3) and (4). Indeed, equation (4) represents the facts for potassium chloride in aqueous solution at much higher concentrations than any of the others, except equation (1) with its unlimited supply of arbitrary constants, but in doing so it would seem to prove too much, since it applies in regions of concentration for which the Debye-Hückel theory itself is not valid. Nevertheless, Ferguson and Vogel have effectively refuted the claim that the *simple* square-root formula of Kohlrausch best represents the dependence of the conductivity of strong electrolytes on concentration, and they have done yeoman service by their resolute appeal to the test of experiment at a time when theoretical formulæ are being applied sometimes with more enthusiasm than discretion.

#### *Equilibria between Gases.*

S. W. Saunders<sup>78</sup> has collected and analysed the available data on the molecular heats of gases, heats of reaction, and chemical and equilibrium constants for ten well-known reactions involving carbon, hydrogen, oxygen, and nitrogen. The results obtained should be of value in the study of fuel-gas production, reactions in the cylinders of internal-combustion engines, detonation of high explosives, etc. The method employed was to fit equations empirically to the molecular heat-temperature curves in each case, and then, by integrating the van 't Hoff isochore and applying the Nernst heat theorem, to calculate the best values for the equilibrium constants. Since the available data are not critically accurate, the Nernst conventional chemical constants were used for the calculation. Where chemical constants were not available, they were calculated either by the van der Waals-Nernst equation or by the Trouton-Nernst rule. In general, the equations obtained for the equilibrium constants agree well with the experimental figures when these are available, and the results agree on the whole with those published by G. N. Lewis and M. Randall.<sup>79</sup> J. R. Partington and W. G. Shilling<sup>80</sup> have critically surveyed the figures for the water-gas equilibrium

<sup>78</sup> S. W. Saunders, *J. Physical Chem.*, 1924, 28, 1151; *A.*, 1924, ii, 836.

<sup>79</sup> "Thermodynamics," McGraw-Hill, 1923.

<sup>80</sup> *J. Soc. Chem. Ind.*, 1925, 44, 149t, 242t.

and, by following substantially the same procedure except that they used experimental values and did not apply the Nernst theorem, obtained the following equation :

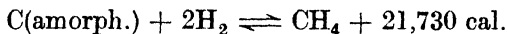
$$\log_{10} K = -2125/T + 1.077 \log_{10} T - 0.000898T + 0.000000133T^2 - 0.5425$$

where  $K = p_{\text{CO}_2} \cdot p_{\text{H}_2} / p_{\text{CO}} \cdot p_{\text{H}_2\text{O}}$ . The agreement of Saunders's figures with those of Partington and Shilling is illustrated below :

$T^\circ \text{ K.}$ .....	1000	1200	1400	1600	1800
$K$ (Saunders) .....	0.71	1.29	2.04	2.95	3.72
$K$ (P. and S.) .....	0.63	1.31	2.15	3.05	3.97
$K$ (exptl.) .....	0.65	1.32	2.08	2.95	3.80

All the above values refer, of course, to true equilibrium which takes some time to obtain. In actual combustion practice, the gases are rarely in contact for a sufficiently long period of time for the attainment of true equilibrium. It has been found, however, by R. T. Haslam<sup>81</sup> from his own results and those of other workers, that in actual water-gas producers, a false equilibrium corresponding fairly well to  $K' = 0.096L$ , where  $L$  is the depth of the fuel bed in feet, is attained.

R. C. Cantelo<sup>82</sup> has investigated the equilibrium



both theoretically and experimentally. In the theoretical investigation he takes account of ten possible reactions involving methane, ethane, ethylene, acetylene, benzene, carbon, and hydrogen, and, by an application of the Nernst approximation formula, shows that in all cases the final equilibrium system consists of methane, carbon, and hydrogen, with less of the first as the temperature rises. He confirms the equation deduced by Saunders (*loc. cit.*) and shows that the apparent disagreement between the earlier results of Mayer and Altmayer,<sup>83</sup> Bone and Coward,<sup>84</sup> and Coward and Wilson<sup>85</sup> may be reconciled by the use of the above value for the heat of reaction with amorphous carbon, in place of the value 18,500 cal./g.-atom for graphite. In order to attain equilibrium in a reasonable time, it is necessary to use an active catalyst (nickel in this instance) and to pass the gaseous mixture repeatedly over it. From the results obtained, the free-energy decrease for the above reaction is calculated to be  $-\Delta F_{298} = 14,500 \text{ cal.}$ , which, combined with the value  $-\Delta F_{298} = 12,800 \text{ cal.}$

<sup>81</sup> *Ind. Eng. Chem.*, 1924, **16**, 782.

<sup>82</sup> *J. Physical Chem.*, 1926, **30**, 1641; 1927, **31**, 124, 246, 417; *A.*, 20, 204, 321, 322.

<sup>83</sup> *Ber.*, 1907, **40**, 2134; *A.*, 1907, i, 457.

<sup>84</sup> *J.*, 1908, **93**, 1197.

<sup>85</sup> *J.*, 1919, **115**, 1380.

given by Lewis and Randall<sup>86</sup> for the same reaction using graphite, leads to  $C(\text{amorph.}) = C(\text{graph.})$ ;  $-\Delta F_{298} = 1700$  cal. F. E. C. Scheffer, T. Dokkum, and J. Al<sup>87</sup> obtain results by a similar method which are in even better agreement with Saunders's equation for the dissociation of methane and point out that, at lower temperatures with a nickel catalyst, a carbide of nickel is formed which alters the equilibrium equation by changing the heat of reaction.

R. W. Fenning and H. T. Tizard<sup>88</sup> have investigated the dissociation of carbon dioxide at high temperatures and pressures comparable with those obtained in internal combustion engines. The method employed was to explode standard mixtures of nitrogen and oxygen containing various amounts of carbon monoxide at constant initial temperatures and pressures. In this way they were enabled to determine the carbon monoxide-oxygen ratio giving the maximum pressure at any temperature, and could vary the temperature by varying the nitrogen-oxygen ratio. They find that the carbon monoxide-oxygen ratio has little effect on the explosion pressure, thus indicating considerable dissociation of carbon dioxide under the conditions of their experiments (30 atm. pressure and  $3000^{\circ}\text{K.}$ , approximately). Their results are expressed by the equation

$$\log K_p = \log p_{\text{CO}}^2 \cdot p_{\text{O}_2} / p_{\text{CO}_2}^2 = 8.46 - 28,600/T,$$

which gives results considerably lower than the accepted values.

The usual procedure, the calculation of equilibrium data from molecular heats and heats of reaction, has recently been reversed by W. G. Shilling,<sup>89</sup> who has calculated the molecular heats of nitrogen, oxygen, nitric oxide, carbon monoxide, carbon dioxide, and ammonia from considerations of various gaseous equilibria in which these gases participate. The results are in good agreement with the accepted data.

H. Ingleson<sup>90</sup> has investigated the thermal dissociation of carbonyl chloride at temperatures between  $360^{\circ}$  and  $480^{\circ}$  by two methods, chemical analysis of the products of dissociation after heating to a constant temperature, and physical measurement of the increase of pressure on dissociation under the same conditions. It was found that the carbon monoxide and chlorine produced by the dissociation were not equivalent when the carbonyl chloride was heated in glass vessels, and this was traced to the attack of the glass

<sup>86</sup> "Thermodynamics," p. 572.

<sup>87</sup> *Rec. trav. chim.*, 1926, **45**, 803; **A.**, 1927, 29.

<sup>88</sup> *Proc. Roy. Soc.*, 1927, [**A**], **115**, 318.

<sup>89</sup> *Trans. Faraday Soc.*, 1926, **22**, 377; **A.**, 1927, 12.

<sup>90</sup> *J.*, 1927, 2244.

by the chlorine. Quartz vessels gave satisfactory results. A linear relationship is found to exist between  $\log K$  and  $1/T$ , and a value is deduced for the heat of dissociation at constant pressure of  $-25,500$  cal. in good agreement with the value obtained by Thomsen. Little change in this value occurs with change of temperature.

P. G. Colin and H. V. Tartar<sup>90a</sup> have investigated the formation of nitric oxide in the high-tension arc and agree with the view expressed by Daniels, Keene, and Manning<sup>90b</sup> that the "temperature" of an electric discharge has no thermodynamic significance, since some molecules become charged and accelerated by the field so that the Maxwell distribution of velocities is no longer obtained. In any case there is a region in the immediate vicinity of the discharge with a lower temperature, which, however, is still high enough to ensure rapid attainment of equilibrium. Provided that this temperature is taken as the thermodynamically significant one, the authors maintain that the law of mass action holds approximately for this reaction in the high-tension arc at pressures greater than half an atmosphere. It is considered that the equilibrated mixture is "frozen" so rapidly after leaving the arc that the use of water-cooled surfaces for this purpose is futile.

#### *Combustion and Flame.*

Considerable attention is being paid at present to radiation and ionisation effects in combustion processes. W. A. Bone and his collaborators have greatly extended their work on gaseous explosions at high pressures, following the course of the explosion by photographically recorded time-pressure curves. The marked difference between the rapid explosions of hydrogen-air mixtures as compared with the comparatively slow explosion of carbon monoxide-air mixtures at 50 atm. initial pressure was originally tentatively explained<sup>91</sup> as being due to the fact that in the former case the energy of reaction was released entirely in a kinetic (temperature) form, thus accelerating the reaction, which proceeded rapidly to equilibrium and was immediately followed by cooling by the walls of the apparatus. In the second case, it was considered that the nitrogen absorbed some of this energy and stored it for a time in a potential form (activation), thus causing the reaction to proceed more slowly, but that this energy was afterwards released in the form of heat, thus delaying the cooling. Subsequent work has confirmed this view in a striking manner. Mixtures of carbon

<sup>90a</sup> *J. Physical Chem.*, 1927, **31**, 1539.

<sup>90b</sup> *Trans. Amer. Electrochem. Soc.*, 1923, **44**, 247.

<sup>91</sup> *Ann. Reports*, 1923, **20**, 20.

monoxide and oxygen with no nitrogen present behave just like hydrogen-oxygen mixtures,<sup>92</sup> and the addition of small quantities of hydrogen to carbon monoxide-air mixtures is sufficient to change the character of the explosion to the hydrogen-air type. This latter effect is explained by the theory that the hydrogen first burns to steam, which then oxidises the carbon monoxide so that none of the characteristic carbon monoxide-oxygen radiations (which alone are absorbed by the nitrogen) is emitted. This is further confirmed by experiments carried out by F. R. Weston<sup>93</sup> on the spectra of carbon monoxide-air and carbon monoxide-hydrogen-air flames. The former show the characteristic blue colour and continuous spectrum of burning carbon monoxide, but as more hydrogen is added the blue colour and the continuous spectrum disappear and steam lines appear in the spectrum until, when equimolecular proportions of carbon monoxide and hydrogen are present, the appearance and spectrum of the flame are practically those of hydrogen.

The effect of increasing initial pressure on the rapidity of the explosion was further studied,<sup>94</sup> and it was found that hydrogen-air and carbon monoxide-oxygen mixtures show increasing rapidity with increasing pressure, but that carbon monoxide-air mixtures show the reverse effect. This would be expected, since increase of pressure increases the density and hence the absorbing capacity of the nitrogen present, and results in the fact that carbon monoxide-air and hydrogen-air mixtures behave similarly at lower pressures. Further evidence in support of the main hypothesis is obtained from the observation<sup>95</sup> that, with excess air, carbon monoxide-air mixtures give quantities of oxides of nitrogen in excess of the thermodynamic yield calculated for nitrogen-oxygen mixtures alone. This would be expected if the carbon monoxide-oxygen reaction activates the nitrogen. Other diluents, except possibly helium,<sup>96</sup> have little or no effect on the carbon monoxide-oxygen reaction. Finally, direct confirmation of the theory was obtained by a spectrographic examination of the ultra-violet radiation emitted during the explosion.<sup>97</sup> Marked absorption was observed when nitrogen or excess carbon monoxide was present, and the absence of bands due to oxides of nitrogen shows that the formation of these compounds is a secondary and later reaction. The

<sup>92</sup> W. A. Bone, D. M. Newitt, and D. T. A. Townend, *Proc. Roy. Soc.*, 1923, [A], **103**, 205; *A.*, 1924, ii, 398.

<sup>93</sup> *Ibid.*, 1925, [A], **109**, 176, 523; *A.*, 1925, ii, 928; *A.*, 1926, 8.

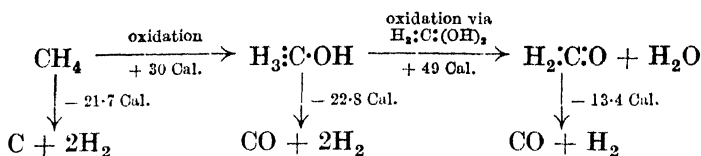
<sup>94</sup> W. A. Bone, D. M. Newitt, and D. T. A. Townend, *ibid.*, 1924, [A], **105**, 406; *A.*, 1924, ii, 398.

<sup>95</sup> *Idem*, *ibid.*, 1925, [A], **108**, 393; *A.*, 1925, ii, 800.

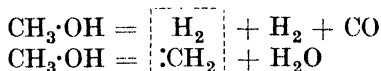
<sup>96</sup> *Idem*, *ibid.*, 1926, [A], **110**, 645; *A.*, 1926, 480.

W. A. Bone and D. M. Newitt, *ibid.*, 1927, [A], **115**, 41.

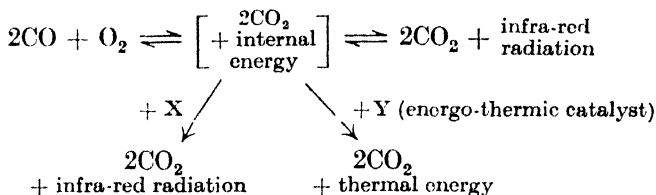
experiments have been extended to the explosion of methane-oxygen mixtures,<sup>98</sup> and it is found that nitrogen is not activated in this case. The results support the following scheme of reaction :



with the possibility of



occurring at lower temperatures. The main conclusions obtained from the above research have been confirmed by C. F. R. Harrison and J. P. Baxter,<sup>99</sup> who followed the course of the reactions by means of temperature measurements. W. E. Garner and C. H. Johnson<sup>1</sup> have studied the effect of the addition of various substances on the infra-red radiation emitted by the carbon monoxide-oxygen reaction. They find that small quantities of water, ethyl iodide, or ethyl nitrate accelerate the explosion and depress the amount of infra-red emission, and that carbon tetrachloride and nitrogen peroxide have the opposite effect. They suppose that the acceleration of the reaction is caused by the conservation of the energy within the system and that the dissipation of the energy by infra-red radiation has the opposite effect. They propose the term *energo-thermic catalysis* for this conserving phenomenon and suggest the following scheme :



G. L. Wendt and F. V. Grimm<sup>2</sup> employ Sir J. J. Thomson's suggestion that an explosive flame is propagated by the emission of electrons from the reacting molecules and that the advance of these electrons before the flame front ionises and activates the unburnt molecules, ultimately causing detonation at high temperatures and pressures. They suggest that "anti-knocks" produce their effects

<sup>98</sup> D. T. A. Townend, *Proc. Roy. Soc.*, 1927, [A], **116**, 637; **A.**, 1146.

<sup>99</sup> *Phil. Mag.*, 1927, [vii], **3**, 30.

<sup>1</sup> *Ibid.*, p. 97.

<sup>2</sup> *Ind. Eng. Chem.*, 1924, **16**, 890.

by removing these electrons. A considerable amount of work has been done on this problem, and W. E. Garner<sup>3</sup> has summarised our knowledge of explosion reactions from this point of view. In collaboration with S. W. Saunders<sup>4</sup> he has studied thermal ionisation in gas explosions and gas reactions. The Saha equation<sup>5</sup>

$$\log K_p = -5048V/T + 2.5 \log T - 6.56$$

is applied to the ionisation of gases in explosions, and it is pointed out that, although the heat of ionisation (represented by the first term) may be as large as 350,000 cal. (corresponding to an ionisation potential of about 15 volts), yet, since the thermal energy liberated by chemical means during the explosion cannot be distributed instantaneously amongst the molecules present, the Maxwell distribution of energy may be momentarily disturbed and there may be more molecules with large energy content than the law predicts. In effect, this implies a reduction of the energy required for ionisation, so that  $K_p$  will be larger than the Saha equation predicts. In order to decide this point, measurements were made of the electrical conductivity of exploding mixtures of hydrogen and oxygen.<sup>6</sup> It was found that the results agreed as closely as could have been expected with the Saha equation, so that little, if any, of the ionisation was due to chemical energy supplied as such and not thermally. The addition of anti-knocks was found to diminish materially the electrical conductivity of such mixtures. S. W. Saunders<sup>7</sup> finds that the increase of conductivity of an exploding mixture of hydrogen and oxygen in a spherical bomb is directly proportional to the distance travelled by the explosion wave in the firing tube. He suggests that this is caused by the increase of ionisation consequent on the rise of temperature due to the influx of hot gases or flame from the firing tube. With K. Sato<sup>8</sup> he has studied explosions of carbon monoxide-oxygen mixtures in a similar manner, and finds that the addition of hydrogen or water to the dry gases materially increases the ionisation produced during the explosion, but that the duration of the ionisation is much greater when dry gases are used, this being in agreement with the longer time of explosion (*i.e.*, the slower development of pressure) in this case. He has also investigated methane-oxygen and acetylene-oxygen mixtures,<sup>9</sup> and finds that the maximum electrical conductivity occurs in the former case when the hydrocarbon is burned to carbon dioxide and water, and in the latter when burned to carbon monoxide and water. J. A. J. Bennett<sup>10</sup> has

<sup>3</sup> *Trans. Faraday Soc.*, 1926, **22**, 253.

<sup>5</sup> *Ann. Reports*, 1923, **20**, 5.

<sup>6</sup> *Trans. Faraday Soc.*, 1926, **22**, 253.

<sup>8</sup> *Ibid.*, p. 248.

<sup>9</sup> *Ibid.*, p. 256.

<sup>4</sup> *Ibid.*, p. 281.

<sup>7</sup> *Ibid.*, 1927, **23**, 242.

<sup>10</sup> *Ibid.*, p. 307.



measured the electrical conductivity of various flames, and has studied the effect of the addition of various substances thereon. He finds that, although ionisation accompanies detonation, it is not related to it. This is confirmed by S. C. Lind,<sup>11</sup> who agrees with W. H. Charch, E. Mack, and C. E. Boord<sup>12</sup> that ionisation accompanies, but does not cause, detonation.

Ionisation has also been found to accompany slow combustion,<sup>13</sup> and J. A. J. Bennett and E. W. J. Mardles<sup>14</sup> have shown that detectable ionisation does not precede chemical change, and that anti-knocks increase the temperature of first detectable ionisation. On this account they are inclined to favour the theory that peroxides<sup>15</sup> are formed immediately prior to combustion, since the complete scission of the oxygen molecule required by the hydroxylation theory might be expected to produce a more copious supply of electrons. J. S. Lewis,<sup>16</sup> however, finds that for paraffin hydrocarbon-air mixtures there exists a critical temperature at which rapid chemical action takes place with an increase in the number of molecules, and considers that his results support the hydroxylation theory. A. Egerton and S. F. Gates<sup>17</sup> find that anti-knocks do not appreciably affect the detonation of acetylene-air or pentane-air mixtures at ordinary or high temperatures and pressures (230°, 10 atm.), but that they do retard the rate of slow combustion of pentane.<sup>18</sup> They point out that "knocking" is associated with a vibratory form of combustion and not with detonation. Similar conclusions as to the effect of anti-knocks on the combustion of hydrocarbons are reached by W. G. Lovell, J. D. Coleman, and T. A. Boyd.<sup>19</sup>

The general conclusions appear to be that gaseous ionisation is a thermal, and not a chemical effect, that there is little, if any, connexion between ignition temperature and ionisation, or between ionisation and detonation, and that therefore Wendt and Grimm's hypothesis is at fault.

The law of flame speeds<sup>20</sup> has been reiterated by W. Payman and R. V. Wheeler,<sup>21</sup> but has been subjected to examination and

<sup>11</sup> *Trans. Faraday Soc.*, 1926, **22**, 291.

<sup>12</sup> *Ind. Eng. Chem.*, 1926, **18**, 334; **B.**, 1926, 570.

<sup>13</sup> J. A. J. Bennett, *Trans. Faraday Soc.*, 1927, **23**, 295.

<sup>14</sup> *J.*, 1927, 3155.

<sup>15</sup> H. L. Callendar, *Engineering*, 1927, **123**, 147.

<sup>16</sup> *J.*, 1927, 1555.

<sup>17</sup> *Proc. Roy. Soc.*, 1927, [*A*], **114**, 137, 152; **A.**, 318.

<sup>18</sup> *Ibid.*, 1927, [*A*], **116**, 516.

<sup>19</sup> *Ind. Eng. Chem.*, 1927, **19**, 373.

<sup>20</sup> *Ann Reports*, 1922, **19**, 20.

<sup>21</sup> *Trans. Faraday Soc.*, 1926, **22**, 301.

severe criticism by W. A. Bone, R. P. Fraser, and D. A. Winter.<sup>22</sup> These authors conclude that it does not hold generally, since it is demonstrably false for both slow- and fast-burning mixtures of complex hydrocarbon, hydrogen, and oxygen (or air). In the same paper, the validity of the suggestion<sup>23</sup> that, with central ignition in a spherical vessel, the maximum explosion pressure is developed at the instant of contact of the flame front with the walls is questioned. It would seem, however, that there is no doubt about this fact, since O. C. de C. Ellis and R. V. Wheeler<sup>24</sup> have published convincing photographs which show that, provided the flame front travels quickly enough to eliminate convection effects, the instants of maximum pressure and of flame contact with the walls of a spherical vessel do coincide. With a cubical vessel under similar conditions, this result would hardly be expected, and it is found in fact that pressure continues to be developed after contact. The same authors have studied ignition of gases in cylindrical and spherical vessels<sup>25</sup> and find in all cases a luminous region behind the flame front. They ascribe this to the "after-burning" of combustible gas left behind by the flame front, and conclude that, although the explosion is complete at the instant of maximum pressure, the combustion process continues for some time afterwards.

#### *The Catalytic Catenary.*

Continuing their previous work<sup>25a</sup> on the catalytic minimum-velocity point in the iodine-acetone reaction, H. M. Dawson and his co-workers<sup>26</sup> have obtained results supporting the "dual" theory of catalysis in an extended form. They have shown that the velocity of this reaction, when occurring in acetic acid-sodium acetate buffer solutions, is influenced, not only by the hydrogen-ion concentration, but also by the concentrations of other ions and molecules in the solutions. (The word concentration in this section means molar concentration uncorrected by any thermodynamic activity factor.) The velocity equation then becomes :

$$v = v_h + v_m + v_a + v_{OH} = k_h[H^+] + k_m[HA] + k_a[A^-] + \frac{k_{OH}}{k_{OH}[OH^-]} \quad (1)$$

terms for the hydrogen and hydroxyl ions, the acid anion, and the undissociated acid molecule entering the velocity equation, but the

<sup>22</sup> *Proc. Roy. Soc.*, 1927, [A], **114**, 420.

<sup>23</sup> *J.*, 1923, **123**, 1257.

<sup>24</sup> *J.*, 1927, 153; compare *J.*, 1925, **127**, 760, 764.

<sup>25</sup> *J.*, 1927, 310.

<sup>25a</sup> *Ann. Reports*, 1926, **23**, 86.

<sup>26</sup> H. M. Dawson and C. R. Hoskins, *J.*, 1926, 3166; H. M. Dawson, *J.*, 1927, 213, 458, 756, 1146, 1290; H. M. Dawson and W. Lowson, *J.*, 1927, 2107, 2444; H. M. Dawson and C. R. Hoskins, *Proc. Leeds Phil. Lit. Soc.*, 1926, **1**, 108; *A.*, 1927, 117.

metallic kation of the salt of the acid is without effect. If the acid concentration ( $c$ ) in the buffer solution is kept constant and the hydrogen-ion concentration of the solution is sufficiently great to allow the effect of the hydroxyl ion to be neglected, and assuming that dissociation of the salt in the buffer mixture is complete and that the ionic dissociation of the acid (dissociation constant =  $K$ ) follows the simple mass law (again without activity factors), it can readily be shown that the velocity is a minimum when

$$[H^+]_i = \sqrt{k_a K c / (k_h - k_m)} \quad . \quad . \quad . \quad (2)$$

and

$$v_i = 2\sqrt{(k_h - k_m)k_a K c} + k_m c \quad . \quad . \quad . \quad (3)$$

from which it follows that the velocity- $p_H$  curve is symmetrical about  $p_{H_i}$ . As the acid concentration is constant, the velocity due to the ions alone is given by

$$u = v_h + v_a = (k_h - k_m)[H^+] + k_a K c / [H^+]$$

This may be transformed to a general form by an application of the method used to obtain a reduced equation from a specific equation of state. Expressing  $[H^+]$  in terms of  $[H^+]_i$  ( $[H^+] = n[H^+]_i$ ) and  $u$  in terms of  $u_i$  ( $u = r u_i$ ), an equation is obtained,  $r = u/u_i = \frac{1}{2}(n + 1/n)$ , between the reduced hydrogen-ion concentration and the reduced ionic velocity, which, since  $\log n = \log [H^+] - \log [H^+]_i = p_{H_i} - p_H = \Delta p_H$ , becomes  $r = \frac{1}{2}(10^{\Delta p_H} + 10^{-\Delta p_H})$ , the equation to a catenary.

This appears to be independent of the nature and concentration of the catalysing acid, the nature of the solvent, and the nature of the reaction. Exactly the same equation is obtained by similar considerations applied to the catalytic effect of water and its ions alone and, since in this case  $k_m$  is possibly very small compared with  $k_{OH}$  and  $k_h$ , the ionic velocity,  $u$ , is identical with the measured velocity  $v$ . The isocatalytic data in this case are obtained from (2) and (3) by equating terms relating to HA to zero, and replacing terms in  $A^-$  by terms in  $OH^-$ , giving:

$$[H^+]_i = \sqrt{k_{OH} K_w / k_h} \quad . \quad . \quad . \quad (4)$$

and

$$v_i = 2\sqrt{k_h k_{OH} K_w} \quad . \quad . \quad . \quad (5)$$

In fact, there appears to be no valid reason for treating the hydroxyl ion in a different manner from other acid anions as regards its catalytic properties.

If the ionic velocity equation be written

$$u = \frac{u_i}{2}(10^{\Delta p_H} + 10^{-\Delta p_H}) = \frac{u_i}{2}([H^+]/[H^+]_i + [H^+]_i/[H^+]),$$

it will be seen that  $u$  depends on  $[H^+]$ ,  $u_i$ , and  $[H^+]_i$ . Since the

last two are functions of the nature and the concentration of the acid alone, a complete representation of the equation is possible in three dimensions. Taking  $u$ ,  $p_H$ , and  $c$  as the variables, and plotting rising values of  $u$  from bottom to top, rising values of  $p_H$  from left to right and rising values of  $c$  from front to back, the catalytic catenary surface appears as a U-shaped valley<sup>27</sup> with a definite boundary to the left and in the front. The left-hand boundary of each section of the surface parallel to the  $u$ - $p_H$  plane (sections of constant  $c$ ) terminates at a point corresponding to salt-free acid, and at higher values of  $c$  ends obviously at lower  $p_H$  values. The projection of these terminal points on the  $u$ - $c$  plane is a parabolic curve, whereas on the  $p_H$ - $c$  plane it is logarithmic. The valley becomes narrower towards the back (as  $c$  increases), but the widths of the valley sections measured at their left-hand terminal points are constant and depend only on the nature of the acid. Loci of points of equal reduced hydrogen-ion concentration (reduced isohydric curves) run along the valley approximately from front to back. The front termination of the valley is obviously the catenary ( $c = 0$ ) characteristic of the catalytic effects of hydrogen and hydroxyl ions alone. Finally, the  $u$ - $p_H$ - $c$  surface may be transformed into a  $v$ - $p_H$ - $c$  surface by lifting it vertically at each left-to-right section by an amount equal to  $k_m c$ .

If the conditions are such that the catalytic effect of the hydroxyl ions cannot be ignored, the mathematical treatment is the same, amounting in effect to the introduction of terms involving  $\text{OH}^-$  and  $\text{H}_2\text{O}$  corresponding to the terms in (2) and (3) which involve  $\text{A}^-$  and  $\text{HA}$ . A compound catenary is then obtained with the isocatalytic data

$$[\text{H}^+]_i = \sqrt{(k_a K c + k_{\text{OH}} K_w) / (k_n - k_m)} \quad . \quad . \quad (6)$$

and

$$v_i = 2\sqrt{(k_n - k_m)(k_a K c + k_{\text{OH}} K_w) + k_m c + K_w c_w} \quad . \quad (7)$$

There is thus a continuous series of compound catenaries of this third type between the  $\text{H}^+$ - $\text{A}^-$  catenaries of the first type and the  $\text{H}^+$ - $\text{OH}^-$  catenary, i.e., equations (2) and (3) represent the limiting case for large acid concentrations, (4) and (5) for  $c = 0$ , and (6) and (7) for intermediate conditions.

These considerations have been successfully applied to velocity measurements, not only of the iodine-acetone reaction, but also of the hydrolysis of ethyl acetate in acetic acid-sodium acetate buffers. T. M. Lowry and G. F. Smith<sup>28</sup> have applied them to the mutarotation of dextrose and have found a small but measurable catalytic activity in the kation of a weak nitrogenous base. T. M. Lowry<sup>29</sup>

<sup>27</sup> *J.*, 1927, 756.

<sup>28</sup> *Ibid.*, p. 2539.

<sup>29</sup> *Ibid.*, p. 2554.

has explained the catalytic effects of various ions and molecules in terms of an electrolytic theory. H. M. Dawson<sup>30</sup> has pointed out that the experimental results obtained by him and his collaborators are entirely at variance with the proton theory of catalysis advanced by F. O. Rice,<sup>31</sup> according to which the catalytic minimum of reactions affected by both the hydrogen and hydroxyl ions should lie at about  $p_H = 5$ . Equation (4) shows that at a given temperature, and therefore at a fixed value of  $K_w$ , the hydrogen-ion concentration of the minimum point is determined by the ratio of the velocity coefficients  $k_{OH}$  and  $k_h$ . This ratio varies widely according to the nature of the reaction, and a variation of  $1 : 10^6$  is by no means extreme. This corresponds to a change in  $[H^+]_i$  of  $1 : 1000$ , and to a change in the  $p_H$  value of the isocatalytic point of 3 units. The proton theory has also been criticised on somewhat similar lines by M. Bergstein and M. Kilpatrick, jun.,<sup>32</sup> and by M. Bergstein.<sup>33</sup>

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<sup>30</sup> *J. Physical Chem.*, 1927, **31**, 1400; **A.**, 1038.

<sup>31</sup> *Ann. Reports*, 1926, **23**, 36.

<sup>32</sup> *J. Physical Chem.*, 1926, **30**, 1616; **A.**, 1927, 214.

<sup>33</sup> *Ibid.*, 1927, **31**, 178; **A.**, 321.

## INORGANIC CHEMISTRY.

IN preparing the Report for 1927 it has been found, as in previous years, that much work of interest and importance has perforce to be omitted. Three subjects have been chosen for special consideration in the earlier paragraphs, and at the end of the Report a list of the systems investigated during the year has been given. Otherwise, the scheme used in previous years has been followed.

### *Valency.*

An important contribution to the theory of chemical combination has been made by N. V. Sidgwick in his Presidential Address to Section B of the British Association Meeting at Leeds. In addition to the generally accepted forms of linkage (*a*) electro-valent, in which electrons are transferred from one atom to another, and (*b*) co-valent, in which the unit linkage consists of two shared electrons derived one from each of the linked atoms, he postulates a third form of linkage (*c*) co-ordinate, in which the unit linkage consists of two electrons, shared in the manner characteristic of the co-valent linkage, but *both derived from one only of the linked atoms*. This simple extension of accepted views explains all the peculiarities of co-ordination compounds, of which the most important are the ability of apparently saturated molecules such as water or ammonia to combine further, the existence of a valency limit (the co-ordination number) independent of the Periodic Group to which the atom belongs, and the peculiar change in electro-valency that attends the replacement of a univalent radical such as chlorine by a whole molecule such as ammonia.

Although space precludes their detailed consideration here, it is extremely interesting to follow these explanations and their further implications, *e.g.*, with reference to the mechanism of hydrolysis of the chlorides of the non-metals and the great stability of carbon tetrachloride, sulphur hexafluoride, etc.; these are fully and clearly set out in the address and in the author's book,<sup>1</sup> to which the reader is referred.

<sup>1</sup> N. V. Sidgwick, "The Electronic Theory of Valency," Clarendon Press, Oxford, 1927.

*Molecular Association.*

Remarkable results have followed from a new attack on the problem of molecular association by the investigation of the effect of catalysts on the equilibrium between the complex and simple molecules in a liquid. Acetic acid in contact with charcoal, platinum-black, or thoria had a vapour pressure greater than its normal value by 1—2 mm. of mercury. This difference in vapour pressure was increased after a period of heating and diminished after a period of cooling. The vapour pressure of benzene in contact with nickel was increased about 3 mm., that of methyl alcohol with charcoal by 6 mm., and that of ether with charcoal by as much as 40 mm., and other results of the same type have been obtained.

Values for the molecular weights, calculated from surface-tension measurements for liquids in contact with catalysts, seem to show that, except in the case of acetic acid, the molecular complexity is increased by heating the liquid for a short period, but is decreased by a longer period of heating.<sup>2</sup> Similar changes have been observed in the density of water and ether when in contact with such catalysts as carbon and thoria.<sup>3</sup> There is no quantitative relation between the vapour-pressure and surface-tension data, but this is hardly to be expected, for the former depend chiefly upon the presence of lighter molecules in the liquid, while the latter tend rather to measure the complexity of the molecular species which accumulates in the surface.

In extension of the work on intensive drying, it has been found that nitrogen tetroxide, dried by repeated distillation over phosphoric oxide, for a period of 4—6 months, has a vapour pressure greater than the normal value by as much as 25 mm. After a sudden change in the temperature of the dried material, the corresponding change in vapour pressure was established slowly, several hours being required to attain a steady value.<sup>4</sup> New data have been obtained for the vapour pressures of intensively-dried hexane, carbon disulphide, ethyl bromide, and nitrogen peroxide.<sup>5</sup> Dried ammonium chloride has a vapour pressure lower than its normal value, and although internal transformations are not inhibited, the equilibrium is shifted, the shift being greater the higher the temperature. These effects vanish above about 310°, and as the temperature is lowered association in the vapour becomes appreciable at 286° and increases progressively.<sup>6</sup>

<sup>2</sup> H. B. Baker, *J.*, 1927, 949.

<sup>3</sup> J. B. Peel, P. L. Robinson, and H. C. Smith, *Nature*, 1927, **120**, 514; *A.*, 1019.

<sup>4</sup> J. W. Smith, *J.*, 1927, 867; *A.*, 506.

<sup>5</sup> A. Smits, *Z. physikal. Chem.*, 1927, **129**, 33; *A.*, 1027.

<sup>6</sup> *Idem*, *Rec. trav. chim.*, 1927, **46**, 445; *A.*, 819.

*Photosynthesis.*

The work on photosynthesis of organic compounds from carbon dioxide and water, begun some years ago by Baly and his co-workers, has, during the past year, been brought to a stage of quite extraordinary interest and importance. It has now been shown that when aqueous carbonic acid is irradiated with ultra-violet light, a photostationary state is established involving, as one component, a complex aldehyde, the reaction being probably  $6\text{H}_2\text{CO}_3 \rightleftharpoons \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2$ . In attempting to assist the formation of carbohydrates by introducing a reducing agent, it was found that ferrous bicarbonate solution when irradiated<sup>n</sup> deposited ferric hydroxide, and that organic compounds with reducing properties were simultaneously formed; also, it was observed, the reaction occurred primarily upon solid surfaces. Hence experiments were made in which various insoluble solids capable of adsorbing carbon dioxide (aluminium powder, barium sulphate, freshly precipitated aluminium hydroxide, and the basic carbonates of aluminium, magnesium, and zinc) were suspended in water through which a stream of carbon dioxide was passed while the suspension, contained in tubes of quartz or Uviol glass, was subjected to the light from a quartz mercury-arc lamp. Evaporation of the filtered solutions yields organic residues, apparently of the nature of complex carbohydrates. Rigid proof was obtained that the materials used were free from organic impurity, and negative results were obtained in numerous control experiments. The most striking and conclusive of these depended on the fact that aluminium hydroxide, after a few hours, becomes unable to adsorb carbon dioxide: thus, using the same tube, light, water, and carbon dioxide, the same aluminium hydroxide when fresh gave the usual yield of carbohydrate, after 8 hours gave a small yield, and after 24 hours gave no trace of organic residue.

A discovery of still greater importance is that visible light may be used in similar syntheses if the solid suspended in the solution and capable of adsorbing carbon dioxide is *coloured*. Suitable solids are nickel or cobalt carbonates, which must be free from alkali, nitrate, chloride, and sulphate. In this case, one of the products is a carbohydrate which reduces Benedict's solution, gives well-marked Molisch and Rubner reactions, and forms a solid osazone. The total quantity of material photosynthesised, and also its percentage reducing power, is greater than with a white surface in ultra-violet light, probably because, with visible light, there is little chance of photochemical decomposition of the products.

There is, apparently, great similarity between these photochemical processes and those in the living plant, *e.g.*, in that both show



similar fatigue effects and both give quantitative yields of the same order, and a possible mechanism of the process *in vivo* is advanced by the authors.<sup>7</sup> The further developments of this work will be awaited with interest.

#### Atomic Weights.

*Argon.* The most probable weight of a litre of pure argon has been computed to be  $1.7833 \pm 0.0001$  g.; whence the atomic weight  $A = 39.94$  is deduced. Although appreciably higher than that adopted by the German Commission (1923), this is regarded as a minimal value.<sup>8</sup>

*Potassium.* Nephelometric determinations of the ratios  $KCl:Ag$  and  $KCl:AgCl$  give as a mean of 31 concordant results,  $0.691147$  for the former and  $0.520186$  for the latter ratio, whence  $K = 39.104 \pm 0.0014$ .<sup>9</sup> Conversion of potassium nitrate to the chloride by heating in hydrogen chloride gives values for the ratio  $KNO_3:KCl$ , from which, by the use of  $N = 14.008$  and well-ascertained values for the ratios  $AgCl:Ag$  and  $KCl:Ag$ , the following atomic weights are calculated:  $K = 39.104 \pm 0.0007$ ;  $Ag = 107.879 \pm 0.0011$ ;  $Cl = 35.456 \pm 0.0003$ .<sup>10</sup>

*Silver.* The value for silver ( $107.864 \pm 0.0013$ ) obtained by Baker and Riley and previously reported<sup>11</sup> leads to values for chlorine (35.452) and nitrogen (13.999) which are regarded as improbable, and it has been suggested that the low value for the atomic weight could be explained by losses of silver (about 0.1 mg.) occurring through the volatility of the metal at  $1000^\circ$ .<sup>12</sup> In reply, Baker and Riley have pointed out that their experimental conditions preclude loss of silver, that there is no evidence of deposition of silver in the cooler parts of the apparatus, and that the silver, after repeated fusion within the apparatus, attained constancy in weight within 0.01–0.02 mg. They have also obtained direct experimental confirmation that loss of silver by volatilisation did not occur.<sup>13</sup>

The atomic weight of silver has been determined by reducing silver nitrate with hydrogen. Errors due to adsorption of air on the silver nitrate and on the reduced silver were eliminated by effecting

<sup>7</sup> E. C. C. Baly, J. B. Davies, M. R. Johnson, and H. Shanassy, *Proc. Roy. Soc.*, 1927, [A], **116**, 197; **A.**, 1040; E. C. C. Baly, W. E. Stephen, and N. R. Hood, *ibid.*, p. 212; **A.**, 1041; E. C. C. Baly and J. B. Davies, *ibid.*, p. 219; **A.**, 1041.

<sup>8</sup> E. Moles, *Ber.*, 1927, **60**, [B], 134; **A.**, 182.

<sup>9</sup> O. Hönigschmid and J. Goubeau, *Z. anorg. Chem.*, 1927, **163**, 93; **A.**, 806.

<sup>10</sup> E. Zintl and J. Goubeau, *ibid.*, p. 302; **A.**, 806.

<sup>11</sup> *Ann. Reports*, 1926, **23**, 50.

<sup>12</sup> B. Brauner, *Nature*, 1927, **119**, 348, 526; **A.**, 289, 493.

<sup>13</sup> H. B. Baker and H. L. Riley, *ibid.*, p. 348, 703; **A.**, 289, 493.

all weighings and the final fusion of the silver in a vacuum. The atomic weight of nitrogen being taken as 14.008, ten highly concordant determinations give the value  $A_g = 107.879 \pm 0.0014$ .<sup>14</sup>

*Boron.* In continuation of previous work on the variation in the atomic weight of boron derived from different sources,<sup>15</sup> the densities of three samples of boron trichloride, portions of the original materials used in the determination of the ratio  $\text{BCl}_3 : 3\text{Ag}$ , after further purification were compared by the flotation method and the relative atomic weight of the boron in each was calculated. The collected results for the three samples of boron from California, Tuscany, and Asia Minor, respectively, are : by analysis, 10.841, 10.825, and 10.818; from densities of boric oxide, 10.847, 10.823, and 10.818; and from densities of boron trichloride, 10.830, 10.825, and 10.817.<sup>16</sup>

*Scandium.* Scandium chloride, prepared by passing carbon tetrachloride diluted with nitrogen over the oxide at 750—850°, purified by fractional sublimation, and weighed with special precautions for the exclusion of moisture, has been used for a determination of the ratio  $\text{ScCl}_3 : 3\text{Ag}$ . The mean of 9 analyses gave the value  $\text{Sc} = 45.160$ .<sup>17</sup>

*Yttrium.* Yttrium chloride, spectroscopically free from other rare-earth metals, has been used for determinations of the ratio  $\text{YCl}_3 : 3\text{AgCl}$ . The mean of 10 analyses gave the value  $\text{Y} = 88.925 \pm 0.002$ .<sup>18</sup>

*Dysprosium.* Similarly, dysprosium chloride, containing only about 0.1% of holmium, has been used for 7 determinations of the ratio to silver chloride, giving as a mean, after correction for the known impurity,  $\text{Dy} = 162.459 \pm 0.004$ .<sup>19</sup>

*Lead.* The constitution of ordinary lead has been investigated by using lead tetramethyl in the mass spectrograph; three principal lines, 206, 207, 208, of intensities, respectively, 4, 3, 7, are in good agreement with the accepted atomic weight, 207.2, and there is, also, a faint line at 209, and some evidence of lines at 203, 204, and 205.<sup>20</sup>

*Nitrogen.* The average values for the densities of nitrogen at 0°

<sup>14</sup> O. Hönigschmid, E. Zintl, and P. Thilo, *Z. anorg. Chem.*, 1927, **163**, 65; **A.**, 806.

<sup>15</sup> *Ann. Reports*, 1925, **22**, 43; 1926, **23**, 49.

<sup>16</sup> H. V. A. Briscoe, P. L. Robinson, and H. C. Smith, *J.*, 1927, 282; **A.**, 392.

<sup>17</sup> N. H. Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 1642; **A.**, 806.

<sup>18</sup> O. Hönigschmid and A. von Welsbach, *Z. anorg. Chem.*, 1927, **165**, 284; **A.**, 915.

<sup>19</sup> *Idem, ibid.*, p. 289; **A.**, 915.

<sup>20</sup> F. W. Aston, *Nature*, 1927, **120**, 224; **A.**, 806.

and 253.33, 506.67, and 760 mm. pressure (at sea-level, in latitude  $45^\circ$ ) have been accurately determined, and are 0.41667, 0.83348, and 1.25036, respectively. If the value  $PV$  at 1 atmosphere be unity, the values at  $\frac{2}{3}$  and  $\frac{1}{3}$  atmosphere are 1.00011 and 1.00028, respectively, the average value of the coefficient of deviation from Boyle's law between 0 and 1 atmosphere being  $-0.00045$ , a value in agreement with existing data. These results lead to the value 14.007 for the atomic weight of nitrogen.<sup>21</sup>

*Chlorine.* In a complete synthesis of silver chloride, chlorine, weighed as the liquid, was reduced to hydrogen chloride by means of ammonium arsenite, and precipitated with a weighed quantity of pure silver dissolved in nitric acid, and the silver chloride so formed was weighed. As a mean of 9 determinations the ratio  $\text{Cl} : \text{Ag}$  was found to be 0.328668, whence, if  $\text{Ag} = 107.880$ , the atomic weight of chlorine is  $\text{Cl} = 35.457$ .<sup>23</sup> Since the weight of silver chloride differed from the weights of the constituent elements by less than the experimental error, doubts that have been expressed<sup>22</sup> as to the purity of atomic-weight silver seem to be unfounded.

It has further been shown that samples of hydrogen chloride, prepared from the extreme fractions obtained in a fractional distillation of carbon tetrachloride, when used for determinations of the ratio  $\text{Ag} : \text{AgCl}$  gave substantially identical values, whence it appears that ordinary fractional distillation does not effect any appreciable isotopic separation.<sup>23</sup>

Saturated solutions of pure sodium chloride, prepared from four different samples of Alsatian potash minerals, differed in density from one another and from a similar solution prepared from commercial salt by less than the experimental error; thus any difference in the isotope ratio is too small to be detected by the methods used.<sup>24</sup>

### Group I.

Much further work has been done on the reduction of aqueous solutions of metallic salts by hydrogen under pressure.<sup>25</sup> Crystalline hydroxides of aluminium and chromium have been prepared by heating solutions of the corresponding nitrate acidified with nitric acid to between  $320$ — $360^\circ$ , under a pressure of  $200$ — $370$  atmospheres

<sup>21</sup> G. P. Baxter and H. W. Starkweather, *Proc. Nat. Acad. Sci.*, 1926, **12**, 703; *A.*, 1927, 194.

<sup>22</sup> P. A. Guye and E. Moles, *J. Chim. physique*, 1917, **15**, 360; *A.*, 1918, ii, 40.

<sup>23</sup> O. Hönigschmid, S. B. Chan, and L. Birckenbach, *Z. anorg. Chem.*, 1927, **163**, 315; *A.*, 806.

<sup>24</sup> (Miles.) E. Gleditsch and L. Gleditsch, *J. Chim. physique*, 1927, **24**, 238; *A.*, 493.

<sup>25</sup> *Ann. Reports*, 1926, **23**, 53.

of hydrogen, for 12—24 hours. The products resemble diaspore and chrome ochre, respectively. If air be used in place of hydrogen, the product is less crystalline and the yield is not quantitative, a portion of the oxide being converted into chromic acid.<sup>26</sup> The action of hydrogen on solutions of copper formate and acetate between 90—180°, at pressures up to 150 atmospheres, and at acidities up to 12.5*N*, has proved interesting. In neutral solution at 100°, hydrolysis occurs with the separation of copper oxide, which is only with difficulty reduced by hydrogen. The presence of acid represses this hydrolysis and the dissolved cupric salt is reduced to the cuprous state. At moderate hydrogen-ion concentration, the cuprous salt is hydrolysed with precipitation of crystalline cuprous oxide, but here again an increase of acidity inhibits hydrolysis and permits further reduction to metallic copper. At higher temperatures (130—180°), the anions decompose, yielding hydrogen which contributes to the foregoing reactions.<sup>27</sup> Stannic hydroxide is reduced to the stannous state by hydrogen at 300° and 38 atmospheres, and to the metal at 350° and 50 atmospheres. Stannic sulphate at 302° and 162 atmospheres gives successively stannous sulphate and stannous sulphide: the reduction is retarded by the presence of sulphuric acid or a sulphate. Stannic chloride is reduced to stannic oxide at 280—300° and 110 atmospheres, and to metallic tin at higher temperatures. Addition of silver chloride gave, at 380° and 260 atmospheres, mainly basic stannous chloride.<sup>28</sup> As with platinum, the production of metal by the action of hydrogen under pressure on chloroiridate solutions at 100° and 103° is greatest at low concentrations and increases with pressure, temperature, and time. Under similar conditions, iridium is deposited more completely than platinum. In cases of incomplete precipitation, a blue, unstable solution of colloidal iridium is produced.<sup>29</sup>

A quantitative investigation has shown that the output of active hydrogen in a Siemens ozoniser, as measured by the reducing action of the gas on sulphur, varies inversely as the rate of flow of the gas through the apparatus, varies directly with the pressure, and shows no linear relation to the voltage used, being negligible above 70 mm. pressure and below 3000 volts.<sup>30</sup> A thorough examination of the processes previously stated to yield triatomic hydrogen leads to the conclusion that there is no evidence for the existence of this substance. Hydrogen which has been passed through hot palladium,

<sup>26</sup> V. Ipatiev and B. Mouromtsev, *Ber.*, 1927, **60**, [B], 1980; *A.*, 1043.

<sup>27</sup> V. Ipatiev and V. Ipatiev, jun., *ibid.*, p. 1982; *A.*, 1042.

<sup>28</sup> V. Ipatiev and V. Niklaev, *Compt. rend.*, 1927, **185**, 462; *A.*, 950.

<sup>29</sup> V. Ipatiev and J. Andreevski, *ibid.*, p. 357; *A.*, 844.

<sup>30</sup> G. A. Elliott, *Trans. Faraday Soc.*, Jan. 1927, advance proof; *A.*, 187.

or submitted to a silent discharge in an ozoniser, and then passed over sulphur does indeed blacken lead acetate paper, but the same effect is obtained if the passage over sulphur is omitted. A number of substances, including palladium, platinum, copper, and glazed porcelain, when heated in hydrogen at 600—700°, yield hydrogen sulphide, doubtless derived from a small sulphur content in these substances: after prolonged treatment they cease to yield hydrogen sulphide. This accords with the Reporters' experience that the most highly purified samples of magnesia contain a trace of sulphur, which is eliminated as hydrogen sulphide when the magnesia is heated to redness in hydrogen. Similarly, a glass ozoniser which initially yields hydrogen sulphide ceases to do so after it has been in use for a time. The ammonia supposed to be formed by the action of nitrogen upon hydrogen generated from magnesium and acid has been shown to persist if no nitrogen is used and to arise, in fact, from the decomposition of magnesium nitride present as an impurity in the magnesium. No reduction of permanganate or indigo could be obtained with the gas remaining after exploding oxygen with excess of hydrogen, and it was shown that hydrogen subjected to  $\alpha$ -radiation from thorium-*B* and thorium-*C* did not thereafter reduce sulphur.<sup>31</sup>

A new technique for the preparation of hydrogen peroxide has been described, involving the decomposition of sodium peroxide with 20% sulphuric acid, removal of sodium sulphate by crystallisation as decahydrate, and vacuum distillation under specified conditions. It gives a fair yield of 85% peroxide.<sup>32</sup> It has been shown that the decomposition of dust-free samples of hydrogen peroxide heated in smooth vessels is very slow, that solutions containing dust give linear decomposition curves, and that inhibitors evidently act by poisoning the surfaces catalysing the decomposition.<sup>33</sup> By studying the change of pressure at constant volume in a quartz bulb (the results in glass are not reproducible), it has been shown that the hydrogen peroxide vapour, admixed with water vapour and oxygen, evolved from 60% aqueous hydrogen peroxide at 85°, consists of simple non-hydrated molecules. The thermal decomposition at 85° is a reaction of zero order, inhibited by molecular oxygen; so that the decomposition ceases when about 20% of the hydrogen peroxide is decomposed.<sup>34</sup>

<sup>31</sup> F. Paneth, E. Klever, and K. Peters, *Z. Elektrochem.*, 1927, **33**, 102; *A.*, 429; M. Scanavy-Grigorieva, *Z. anorg. Chem.*, 1926, **159**, 55; *A.*, 1927, 119.

<sup>32</sup> M. L. Kilpatrick, O. M. Reiff, and F. O. Rice, *J. Amer. Chem. Soc.*, 1926, **48**, 3019; *A.*, 1927, 120.

<sup>33</sup> F. O. Rice and O. M. Reiff, *J. Physical Chem.*, 1927, **31**, 1352; *A.*, 1035.

<sup>34</sup> L. W. Elder, jun., and E. K. Rideal, *Trans. Faraday Soc.*, 1927, **23**, 545; *A.*, 1035.

Anhydrous lithium iodide decomposes at high temperatures in a stream of oxygen according to the equation  $10\text{LiI} + 5\text{O}_2 \longrightarrow 2\text{LiIO}_3 + 4\text{Li}_2\text{O} + 4\text{I}_2$ .<sup>35</sup> A mono- and a tri-hydrate of lithium chlorate are prepared by seeding solutions corresponding with  $\text{LiClO}_3 \cdot \text{H}_2\text{O}$  and  $\text{LiClO}_3 \cdot 3\text{H}_2\text{O}$  at  $-28^\circ$  and  $-20^\circ$ , respectively, with crystals of the hydrate  $3\text{LiClO}_3 \cdot \text{H}_2\text{O}$ .<sup>36</sup>

The colourless needles of sodium hydride prepared by direct union of hydrogen and sodium belong to the regular system, and X-ray examination by the Debye-Scherrer method shows that the crystal lattice is probably similar to that of rock-salt. The dissociation of the hydride at reduced pressures and at ordinary temperatures is that to be expected with a solution of hydrogen in sodium rather than a definite compound. At higher temperatures, however, the dissociation is accompanied by the separation of sodium, free or almost free from hydrogen.<sup>37</sup>

A simple and convenient method for preparing small quantities of pure potassium, rubidium, or caesium depends on the fact that barium azide, conveniently prepared by distilling azoimide into barium hydroxide, decomposes at  $200^\circ$ ; so that if alkali chlorides are mixed with the azide in solution, and the solution is evaporated to dryness in a vacuum, the solid residue on heating to a moderately high temperature yields a distillate of the alkali metal.<sup>38</sup>

It has been found that the colours shown by a copper oxide film may be made truly homogeneous if special precautions are taken in the preparation and activation of the film. The study of such films affords much evidence that the colours are produced by interference in a thin layer of oxide. The order of production of the colours corresponds with the order tabulated by Rollet for the interference colours of air films of increasing thickness seen by transmitted light. It is found that the fall in electrical conductivity of the oxidised film supported on china clay is proportional to the equivalent air thickness of the oxide film, *i.e.*, to the thickness of an air film which would produce the same colour as the copper oxide film. The equivalent air thickness is approximately proportional to the quantity of metal oxidised. The wave-lengths of the maxima in the absorption or reflexion bands in the spectrum of the light reflected from the film move towards the red as the thickness increases,

<sup>35</sup> J. P. Simmons and C. F. Pickett, *J. Amer. Chem. Soc.*, 1927, **49**, 701; **A.**, 429.

<sup>36</sup> L. Berg, *Z. anorg. Chem.*, 1927, **166**, 231; **A.**, 1042.

<sup>37</sup> G. F. Hüttig and F. Brodkorb, *ibid.*, 1927, **161**, 353; **A.**, 529; compare *Ann. Reports*, 1926, **23**, 53.

<sup>38</sup> J. H. de Boer, P. Clausing, and G. Zecher, *Z. anorg. Chem.*, 1927, **160**, 128; **A.**, 328.

and the absolute thickness of the oxide film, calculated from the density and the mass of oxygen taken up per  $\text{cm}^2$  of the surface, agrees moderately well with the thickness calculated from the position of the absorption band and the corresponding refractive index.<sup>39</sup>

Curves connecting the absorption as a function of the composition in solutions of cupric ion and ammonia in concentrated ammonium nitrate, showed marked maxima, corresponding in the case of equimolecular mixtures to the formula  $\text{Cu}(\text{NH}_3)_4$ . For non-equimolecular solutions, the dissociation constant was calculated, and was found to agree with the result obtained from the absorption data. The tetra-ammonia ion, therefore, is probably the only cupriammonia ion stable at the ordinary temperature.<sup>40</sup> A complex thiosulphate,  $\text{Cu}_{10}\text{S}_{15}\text{O}_{18}, 9\text{NH}_3$ , has been prepared by mixing a solution of sodium thiosulphate in concentrated ammonia with cupric chloride. The substance forms stable deep blue crystals.<sup>41</sup> Unsuccessful attempts have been made to discover the missing element 87 produced by the loss of an  $\alpha$ -particle from mesothorium-2 or as a  $\beta$ -product from radon.<sup>42</sup>

### Group II.

The process of dehydration of the hemihydrate of calcium sulphate above  $80^\circ$  is reversible, but the dehydration does not take place spontaneously. Below  $80^\circ$ , the water-vapour pressure of the system lies below 2 mm. of mercury. The decomposition of the hemihydrate into a mixture of dihydrate and anhydrous salt is therefore thermodynamically impossible, as the regeneration of the hemihydrate could not take place. Such a decomposition is possible only if two forms of the soluble anhydrous salt exist, *viz.*, an  $\alpha$ -form stable below  $72^\circ$  and incapable of existence in equilibrium with the hemihydrate, and a  $\beta$ -form stable above  $72^\circ$  and in the presence of hemihydrate. Dilatometric measurements confirm the existence of two forms: the transition  $\alpha \rightleftharpoons \beta$  occurs at  $82^\circ$ , and is rendered evident also from the nature of the heating and cooling curves, the  $\beta$ -form being produced from the  $\alpha$  with the evolution of heat. These facts constitute a probable explanation of contradictions in the literature concerning the crystal form of anhydrous calcium sulphate.<sup>43</sup>

<sup>39</sup> F. H. Constable, *Proc. Roy. Soc.*, 1927, [A], **115**, 570; **A.**, 930.

<sup>40</sup> P. Job, *Compt. rend.*, 1927, **184**, 204; **A.**, 205.

<sup>41</sup> D. W. Horn and R. E. Crawford, *Amer. J. Pharm.*, 1927, **99**, 274; **A.**, 634.

<sup>42</sup> G. von Hevesy, *Kgl. Danske Videnskab. Selsk. math.-fys. Medd.*, 1926, **7**, No. 11, 1; **A.**, 1927, 289.

<sup>43</sup> D. Balarev [with A. Spassov], *Z. anorg. Chem.*, 1927, **163**, 137; **A.**, 829.

Large, violet mixed crystals of barium sulphate with potassium permanganate, which are not decomposed by oxalic acid in the presence of sulphuric acid or by sulphurous acid, are obtained by allowing 2*N*-solutions of sulphuric acid and barium chloride to diffuse slowly into a 10% solution of potassium permanganate.<sup>44</sup>

Doubt has been thrown upon the volatility of barium sulphate previously reported<sup>45</sup> on the strength of the observations that the salt moistened with sulphuric acid colours the flame of a Bunsen burner green and that the flame obtained by igniting the vapours from a heated mixture of barium nitrate, concentrated sulphuric acid, and methyl alcohol is also green. It has been suggested that the former coloration is due to the formation of a spray of finely divided barium hydrogen sulphate or pyrosulphate, and in the second case it has been shown that the colour is probably due to methyl nitrate, as similar colorations are obtained by substituting strontium or ammonium nitrate for the barium salt.<sup>46</sup>

For the separation of radium from barium, the fractional precipitation of the chromate in 0.05—0.3*N*-acid solutions is as efficient as the bromide method and is advantageous when only small quantities of the mixture are available.<sup>47</sup>

The perchlorates, as drying agents, have been further investigated.<sup>48</sup> Barium perchlorate trihydrate on dehydration in a vacuum at 100—140° gives the anhydrous salt without fusing, and this equals sulphuric acid in drying efficiency. A mixture of barium perchlorate with up to 35% of magnesium perchlorate can be dehydrated at 250° and 102 mm. pressure without fusing; the granules of such a mixture containing 26.5% of magnesium perchlorate in a drying column 15 cm. long and 2.5 cm. in diameter allow only 0.001 g. of water to remain unabsorbed when air 60% saturated with moisture is passed through for 5.5 hours at the rate of 53 litres per hour. The mixture is, therefore, an extremely efficient drying agent.<sup>49</sup>

### Group III.

Molten mixtures of a metallic oxide, boric anhydride or borax, and a fluoride, when electrolysed with high cathode current densities, have yielded in a molten or crystalline state most of the metals with

<sup>44</sup> W. Geilmann and E. Wünnenberg, *Z. anorg. Chem.*, 1927, **159**, 271; **A.**, 120.

<sup>45</sup> F. Krauss, *Chem.-Ztg.*, 1926, **50**, 33; **A.**, 1926, 368.

<sup>46</sup> F. L. Hahn, *ibid.*, p. 934; **B.**, 1927, 106; compare Krauss, ref. 45; F. Krauss, *ibid.*, 1927, **51**, 38; **B.**, 139.

<sup>47</sup> L. M. Henderson and F. C. Kracek, *J. Amer. Chem. Soc.*, 1927, **49**, 738; **A.**, 431.

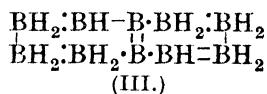
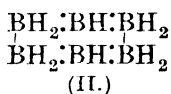
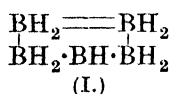
<sup>48</sup> Compare *Ann. Reports*, 1922, **19**, 45.

<sup>49</sup> G. F. Smith, *Ind. Eng. Chem.*, 1927, **19**, 411; **A.**, 438.



heats of oxidation less than that of sodium.<sup>50</sup> A similar method has been applied to the production of boron, the mixture  $2\text{B}_2\text{O}_3 + \text{MgO} + \text{MgF}_2$  being used at  $1100^\circ$ , in a charcoal crucible which acts as anode, the cathode being an iron rod. The cathode deposit, consisting of boron agglomerated by the solidified electrolyte, is ground and extracted with hydrochloric acid, giving a 95% yield of boron of 92% purity.<sup>51</sup>

The constitution of the hydrides of boron, discovered by Stock and his co-workers<sup>52</sup> and formulated by them on the assumption that the valencies involved were 3 and 4, has been reviewed by several authors. It is suggested that a more satisfactory explanation of the compounds may be based on the assumption that the valencies are 3 and 5 and the co-ordination number 4. On this basis,  $\text{B}_2\text{H}_6$  would be formulated  $\text{H}_3\text{B}:\text{BH}_3$ , the ammonia compound either as the salt  $(\text{H}_2\text{B}:\text{BH}_2^-)(\text{NH}_4^+)_2$  or, less probably,  $\text{H}_3\text{B}:\text{NH}_3$ , and the hydride  $\text{B}_4\text{H}_{10}$  as  $\text{H}_3\text{B}:\text{BH}_2\cdot\text{BH}_2:\text{BH}_3$ . The comparatively great stability of hydrides with 5, 6, and 10 boron atoms is most satisfactorily explained by the adoption of ring formulæ as follows:



Formula (I) accounts for the fact that  $\text{B}_5\text{H}_9$  combines with 4 molecules of ammonia to give  $\text{B}_5\text{H}_9(\text{NH}_3)_4$ , which with hydrogen chloride evolves 4 molecules of hydrogen rapidly and a further 3 molecules more slowly. The naphthalene structure of (III) is in agreement with its chemical properties and its high melting point.<sup>53</sup> Electronic interpretations of the constitution of the boron hydrides have been advanced by Ulmann and by Main Smith.<sup>54</sup>

Investigations of the freezing point of boric acid solutions, and of the solubility of the acid in water in the presence of various proportions of hydrogen peroxide, together with the conductivity of these solutions, have thrown little or no light on the constitution of the acid, but conductivity measurements show that the monoborates are binary electrolytes and give no evidence of a ternary dissociation corresponding with formulæ of the type  $\text{M}_2\text{B}_2\text{O}_4$ .

<sup>50</sup> Andrieux, *Compt. rend.*, 1927, **184**, 91; **A.**, 216.

<sup>51</sup> L. Andrieux, *ibid.*, **185**, 119; **A.**, 844.

<sup>52</sup> Compare *Ann. Reports*, 1926, **23**, 58.

<sup>53</sup> J. A. Christiansen, *Z. anorg. Chem.*, 1927, **160**, 395; **A.**, 399.

<sup>54</sup> M. Ulmann, *Ber.*, 1927, **60**, [B], 610; **A.**, 399; but see A. Stock, *Ber.*, 1927, **60**, [B], 1039; **A.**, 714, who regards these explanations as unsatisfactory; see also E. Müller, *ibid.*, p. 1323; compare E. Müller, *Z. Elektrochem.*, 1925, **31**, 382; **A.**, 1925, ii, 841; J. D. Main Smith, *Chem. News*, 1927, **135**, 81; **A.**, 813.

Concentrated solutions of the corresponding diborates apparently contain  $B_4O_7^{''}$  ions, rather than univalent diborate ions. For more dilute solutions, the experimental data are compatible with a decomposition of the diborate into monoborate and free boric acid. In concentrated solutions, the perborates behave as ternary electrolytes, giving the ion  $2BO_2 \cdot 2H_2O_2^{''}$ , whereas dilute solutions apparently contain the ion  $BO_2 \cdot H_2O_2^{'}$ . The fact that pentaborates give unusually high values for van 't Hoff's coefficient,  $i$ , is ascribed to a very considerable decomposition of the pentaborate ion,  $B_5O_8^{'}$ , into less complex ions and boric acid, which occurs even when considerable excess of boric acid is added.<sup>55</sup> The literature relating to those borates of the alkali metals which can be crystallised from aqueous solution has been critically reviewed, and X-ray diagrams and dehydration experiments have shown that the removal of the last molecule of water from the hydrates of sodium monoborate is accompanied by a change in the structure of the crystal. With the diborate it is apparently the last three water molecules which are of structural importance, but the pentahydrate stable above  $60^\circ$  appears to occupy an exceptional position.<sup>56</sup>

A large number of fluoroborates have been prepared, analysed, and described; those of the heavy metals appear to be characterised by their great solubility, deliquescence, and instability at higher temperatures.<sup>57</sup>

A new scaly variety of aluminium hydroxide,  $Al_2O_3 \cdot 4H_2O$ ,  $d_{31}^{31}$  1.5490, soluble in mineral acids, has been produced by the reduction of barium nitrate solution with the aluminium-mercury couple at  $0^\circ$ . One molecule of water is lost at  $100^\circ$ , and the last molecule, with difficulty, at a red heat.<sup>58</sup>

A vigorous discussion continues as to priority in the discovery of element No. 61, but this can hardly be summarised here.<sup>59</sup> It is more important to note that attempts to increase the amount

<sup>55</sup> H. Menzel, *Z. anorg. Chem.*, 1927, **162**, 1, 22; **A.**, 937.

<sup>56</sup> H. Menzel [with J. Meckwitz], *ibid.*, **166**, 63; **A.**, 1043.

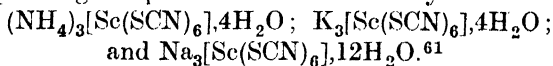
<sup>57</sup> E. Wilke-Dörfurt and G. Balz, *ibid.*, **159**, 197; **A.**, 120; H. Funk and F. Binder, *ibid.*, 1926, **159**, 121; **A.**, 1927, 219.

<sup>58</sup> P. Neogi and A. K. Mitra, *J.*, 1927, 1222; **A.**, 741.

<sup>59</sup> W. Prandtl and A. Grimm, *Z. angew. Chem.*, 1926, **39**, 1333; **A.**, 1927, 9; L. Rolla and L. Fernandes, *Gazzetta*, 1926, **56**, 688; **A.**, 1927, 9; *idem*, *Z. anorg. Chem.*, 1926, **157**, 371; **A.**, 1927, 31; R. Brunetti, *Atti R. Accad. Lincei*, 1926, [vi], **4**, 518; **A.**, 1927, 190; L. Rolla and L. Fernandes, *Gazzetta*, 1926, **56**, 862; *Atti R. Accad. Lincei*, 1926, [vi], **4**, 498; **A.**, 1927, 190; R. Brunetti, *ibid.*, p. 515; **A.**, 1927, 190; W. A. Noyes, *Nature*, 1927, **119**, 319; **A.**, 296; R. Brunetti, *Z. anorg. Chem.*, 1927, **160**, 237; **A.**, 296; L. Rolla and L. Fernandes, *ibid.*, p. 190; **A.**, 296; W. A. Noyes, *Nature*, 1927, **120**, 14; **A.**, 714; L. Rolla and L. Fernandes, *Gazzetta*, 1927, **57**, 290; **A.**, 611; B. S. Hopkins, *J. Franklin Inst.*, 1927, **204**, 1; **A.**, 814.

available for X-ray examination have resulted in the production of a sample containing about 1% of the element which gave seven lines of the *L*-series of illinium.<sup>60</sup>

Scandium acetylacetonate and salts of the types  $M_3(\text{ScF}_6)$  and  $K_3[M(\text{C}_2\text{O}_4)_3] \cdot 5\text{H}_2\text{O}$  strongly resemble those of the trivalent elements of the iron family, and further evidence of this analogy is afforded by the preparation of the new compounds, which are isomorphous with the corresponding compounds of the iron family :



Samarous chloride has been prepared by reducing the anhydrous trichloride in a mixture of ammonia and hydrogen at  $750^\circ$ . It forms a mass of dark reddish-brown needles, m. p.  $740^\circ$ , readily soluble in water to a solution which, on keeping, evolves hydrogen and deposits an insoluble oxychloride. The intense colour of the dichloride may serve to detect samarium in the presence of large quantities of other earths.<sup>62</sup> A number of new compounds of europium have been described, including the oxalate, nitrate, normal and hydrogen tartrates, acetate, citrate, acetylacetonate, iodate, carbonate, and cyanoplatinate.<sup>63</sup> The ammoniates of the chlorides of lanthanum, cerium, praseodymium, and neodymium have been prepared and observations made of their decomposition temperatures and of the contraction in volume attending their formation.<sup>64</sup>

Gallium has been used in a fused quartz thermometer which may be employed to measure temperatures up to  $1000^\circ$ . The removal of gas from the liquid gallium and the effect of impurities on the amount of undercooling and on the tendency to wet quartz have been investigated. The ease of surface oxidation of gallium is greater than is represented in the literature.<sup>65</sup>

#### Group IV.

The vapour pressure of carbon suboxide ( $\text{C}_3\text{O}_2$ ) has been measured between  $-62^\circ$  and  $4^\circ$ , giving a calculated b. p. at atmospheric pressure of  $6.8^\circ$  and a heat of vaporisation of approximately 6 kg.-cal. The pure gas is very stable in contact with dry, clean glass, but decomposes in contact with mercury or glass contaminated with the polymerised form.<sup>66</sup>

<sup>60</sup> J. M. Cork, C. James, and H. C. Fogg, *Proc. Nat. Acad. Sci.*, 1926, **12**, 696; *A.*, 1927, 190.

<sup>61</sup> G. Urbain and P. B. Sarkar, *Compt. rend.*, 1927, **185**, 593; *A.*, 1010.

<sup>62</sup> G. Jantsch, H. Rüping, and W. Kunze, *Z. anorg. Chem.*, 1927, **161**, 210; *A.*, 530.

<sup>63</sup> M. P. B. Sarkar, *Bull. Soc. chim.*, 1927, [iv], **41**, 185; *A.*, 325.

<sup>64</sup> F. Ephraïm and R. Block, *Ber.*, 1926, **59**, [B], 2692; *A.*, 1927, 121.

<sup>65</sup> S. Boyer, *J. Opt. Soc. Amer.*, 1926, **13**, 117; *A.*, 1927, 100.

<sup>66</sup> M. J. Edwards and J. M. Williams, *J.*, 1927, 855; *A.*, 506.

A brown solid, having the composition  $C_5O_3 \cdot xH_2O$ , has been produced by circulating carbon monoxide, at 20–69 cm. pressure and continuously freed from carbon dioxide, through a Siemens ozoniser actuated by alternating electric current of the order of 20,000 volts per cm. at 250 cycles per second. This substance was very hygroscopic, reacted with water, giving approximately 1 mol. of  $CO_2$  per mol. of  $C_5O_3$ , and formed a solution containing oxalic acid (1 mol. per 3 mols.  $C_5O_3$ ), colloidal particles, and a dark insoluble residue.<sup>67</sup>

A long series of experiments on the catalytic synthesis of hydrocyanic acid from nitric oxide and hydrocarbons at high temperatures has led to the general conclusion that the first stage in the reaction is the reduction of nitric oxide to ammonia, part of which reacts to form hydrocyanic acid, whilst part dissociates into hydrogen and nitrogen. Ethylene decomposes gradually, giving methane, hydrogen, and carbon, but acetylene and highly unsaturated hydrocarbon residues ( $CH_2=$  and  $CH\equiv$ ) are probably intermediate products. The formation of hydrocyanic acid is then completed by the action of ammonia either on ethylene or on one of these intermediate products. It is unlikely that solid carbon plays any appreciable part in the reaction. Carbon monoxide is probably produced by the interaction of ethylene with the water vapour formed in the reduction of nitric oxide.<sup>68</sup>

The reactions of alkali thiocyanates which have been strongly acidified with sulphuric acid differ greatly from those of the neutral salt. Thus ferric salts give a red colour which rapidly disappears, whilst the white precipitates obtained with silver, lead, and mercury salts slowly become yellow, and cobalt nitrate yields a green precipitate of perthiocyanogen,  $(HC_3N_3S_3)$ , with traces of cobalt salts and of perthiocyanic acid,  $(H_2C_2N_2S_3)$ . When acids (preferably nitric acid) are added to a solution containing two or more thiocyanates, precipitation of a complex thiocyanate of definite composition may result. The precipitate must be collected immediately; otherwise a violent reaction may take place after a few minutes, with the decomposition of the precipitate and evolution of oxides of nitrogen, sulphur dioxide, hydrogen cyanide, etc. The compounds  $HgCo(CNS)$  (blue) (which may be used as a fairly delicate qualitative test for mercuric ions),  $PbBi(CNS)_5$  (red), and possibly  $CdHgBi(CNS)_7$  (red) have been obtained by this method.<sup>69</sup>

Pure silicon has been prepared by interaction of pure silicon tetrachloride vapour and hydrogen at the surface of a glowing

<sup>67</sup> R. W. Lunt and R. Venkateswaran, *J.*, 1927, 857; **A.**, 531.

<sup>68</sup> E. Elöd and H. Nedelmann, *Z. Elektrochem.*, 1927, **33**, 217; **A.**, 838.

<sup>69</sup> B. Ormont, *Z. anorg. Chem.*, 1927, **161**, 337; **A.**, 531.

carbon filament 0.3 mm. thick, maintained at 1000° by an electric current. The product has a metallic appearance, is very stable in air, and appears to become more brittle as the temperature rises. The coefficient of linear expansion between 18° and 950° is  $3.55 \times 10^{-6}$ ; the electrical conductivity increases with rise in temperature.<sup>70</sup>

The absolute density and coefficient of thermal expansion of silicon tetrachloride have been found to be  $1.481475 \pm 0.0_568/20^\circ$  and  $0.0014044 \pm 0.0_687/20^\circ$ , respectively.<sup>71</sup>

Pure germanium, prepared by reducing specially purified germanium dioxide with hydrogen and graphite, has m. p. 959° in hydrogen, 958° in carbon dioxide, and 975° in a vacuum; it is volatile in hydrogen at atmospheric pressure below 800°, and in a vacuum below 760°. Molten germanium (1 g.) absorbs hydrogen (0.1839 g.) on cooling and reduces germanium dioxide to the monoxide.<sup>72</sup> The metal has also been prepared by reduction of the dioxide with carbon under a flux of sodium chloride in a graphite crucible heated in an induction furnace.<sup>73</sup>

The formation of complex compounds of stannic and stannous iodides with other metallic and organometallic halides has been extensively investigated, and a number of stable compounds have been reported.<sup>74</sup>

The specific heats at 8—13° of chemically and physically pure white and grey tin are reported as  $0.0537 \pm 0.0003$  and  $0.0493 \pm 0.0002$ , respectively,<sup>75</sup> and the transition temperature of the two forms is found to be 13°.<sup>76</sup> It has also been shown that the metal heated at 350° for some minutes gives a calorimetric curve without discontinuities, whilst if heated at 500° for 2 hours, it gives a curve showing a sharp break at 170—171°, which is accentuated by increase in time or temperature. The dependence of such results on the previous thermal treatment of the metal, irrespective of its purity, explains the anomalous results previously obtained.<sup>77</sup>

#### Group V.

The view that active nitrogen is a metastable molecular form with an energy of about 42,500 cal. per g.-mol. (*i.e.*, approximately

<sup>70</sup> R. Hölbling, *Z. angew. Chem.*, 1927, **40**, 655; **A.**, 844.

<sup>71</sup> P. L. Robinson and H. C. Smith, *J.*, 1928, 3152; **A.**, 1927, 102.

<sup>72</sup> J. H. Müller, E. F. Pike, and A. K. Graham, *Proc. Amer. Phil. Soc.*, 1926, **65**, 15; **A.**, 1927, 121.

<sup>73</sup> (Miss) K. M. Tressler and L. M. Dennis, *J. Physical Chem.*, 1927, **31**, 1429; **A.**, 1045.

<sup>74</sup> T. Karantassis, *Ann. Chim.*, 1927, [x], **8**, 71; **A.**, 950.

<sup>75</sup> E. Cohen and K. D. Dekker, *Z. physikal. Chem.*, 1927, **127**, 183; **A.**, 818.

<sup>76</sup> *Idem, ibid.*, p. 178; **A.**, 818.

<sup>77</sup> A. Travers and Huot, *Compt. rend.*, 1927, **184**, 152; **A.**, 194.

2.0 volts)<sup>78</sup> is said to be difficult to reconcile with the spectroscopic data.<sup>79</sup> A study of the reactions of active nitrogen with other gases of varying critical increments, confirmed the energy given above as a mean value, but was held to show that the gas contains three species of active molecules, some having energies just above and others energies just below the mean value.<sup>80</sup> From later experiments, the conclusion is drawn that the glowing and chemically active forms of nitrogen are distinct, the former being due to recombination of atoms with a heat of formation of 250,000 cal./g.-mol., and the latter, which possesses an energy of about 45,000 cal./g.-mol., may be metastable molecular nitrogen or a more complex substance such as  $N_3$ .<sup>81</sup> The decay process, presumably of this form, in contact with metallic filaments is bimolecular and gives an energy value of 46,000 cal./g.-mol.<sup>82</sup> On the other hand, a study of the electrical behaviour of glowing active nitrogen indicates that it is molecular nitrogen in a metastable state with an energy between 9.4 and 10.4 volts.<sup>83</sup>

Sodium azide when rendered unstable thermally in an atmosphere of oxygen is converted almost quantitatively into sodium nitrite and nitrogen. Catalysts or carriers are unnecessary, but the presence of free alkali is essential to delay the transformation  $3NaN \rightarrow Na_3N + N_2$  until the oxygen molecule can penetrate the nitrogen zone. Oxidising agents such as copper oxide, manganese dioxide, and lead dioxide merely facilitate the removal of nitrogen by oxidising the sodium, whereas peroxides such as barium peroxide have the same effect as gaseous oxygen, since they furnish molecular oxygen. It therefore appears probable that the direct combustion of ammonia to nitrite and subsequently to nitrate at a basic contact depends on an unstabilising of the molecule, prior to thermal dissociation, which may be represented by the scheme  $HN \leftrightarrow H_2$ ; molecular oxygen then penetrates the molecule and displaces hydrogen, which is subsequently oxidised to water. In a similar manner, hydrogen converts sodium azide into nitrogen and sodamide, the greater velocity of diffusion allowing it to penetrate the nitrogen zone so rapidly that the presence of alkali is not necessary to prevent the transformation  $3NaN \rightarrow Na_3N + N_2$ . If sodium azide is decomposed in an atmosphere of carbon dioxide, the  $NaN$  residues unite with loss of nitrogen and production of sodium nitride, which is very readily hydrolysed to sodium hydroxide

<sup>78</sup> *Ann. Reports*, 1926, **23**, 65.

<sup>79</sup> R. C. Johnson, *Nature*, 1927, **119**, 9; *A.*, 85.

<sup>80</sup> E. J. B. Willey and E. K. Rideal, *J.*, 1927, 669; *A.*, 431.

<sup>81</sup> E. J. B. Willey, *Nature*, 1927, **119**, 924; *A.*, 635.

<sup>82</sup> E. J. B. Willey, *J.*, 1927, 2188; *A.*, 1038.

<sup>83</sup> P. A. Constantinides, *Physical Rev.*, 1927, [ii], **30**, 95; *A.*, 916.

and ammonia, even when the concentration of aqueous vapour is very low.<sup>84</sup>

The behaviour of nitrogen tetroxide and trioxide in a number of additive compounds with tin and titanium tetrachloride, chosen because the co-ordination number is invariably six, has led to the discovery of certain new compounds stable only at low temperatures and to the conclusion that the oxides may best be represented respectively as  $(\text{O:})_2\text{N}\cdot\text{O}\cdot\text{N}\cdot\text{O}$ , and  $\text{O}\cdot\text{N}\cdot\text{O}\cdot\text{N}\cdot\text{O}$ .<sup>85</sup> A study of the thermal decomposition of nitrogen pentoxide in the presence of foreign gases has shown that hydrogen, carbon monoxide, and bromine are without influence, but that certain organic vapours bring about rapid, almost explosive, reaction; whilst nitric oxide is oxidised immediately. Hydrogen and air have no effect on the photochemical decomposition, but bromine, possibly by optical screening, retards it. The mechanism of the decomposition is considered to be  $\text{N}_2\text{O}_5 \longrightarrow \text{NO} + \text{NO}_2 + \text{O}_2$  (slow);  $\text{NO} + \text{N}_2\text{O}_5 \longrightarrow 3\text{NO}_2$  (rapid).<sup>86</sup>

Since the reaction  $4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{HNO}_3$  involves a diminution in volume, attempts have been made to use nitric acid as a carrier of oxygen present at a high pressure. In this way, with oxygen at 20 atm., sodium nitrite has been oxidised to nitrate and arsenious oxide has yielded arsenic acid; but no change took place in the absence of nitric acid. The method has been applied with success to arsenic sulphides, which are converted into arsenic acid and sulphuric acid.<sup>87</sup>

Nitrogen sulphide has been prepared by passing ammonia mixed with air into an anhydrous benzene solution of sulphur dichloride. It had m. p.  $179^\circ$ ,  $d$  2.2, and  $M$  184.3, corresponding to the accepted formula  $\text{N}_4\text{S}_4$ . It sublimes near the melting point and explodes at higher temperatures. Its solubility in various solvents and its reactions with water, acid, and alkali, respectively, have been fully investigated. The structural formula suggested as according best with its properties is  $\text{S}:\text{S}(\text{N}:\text{S}:\text{N})_2$ .<sup>88</sup>

It is only possible here to refer to papers on the chemiluminescence of phosphorus vapour<sup>89</sup> and on the nature of the ions produced by glowing phosphorus.<sup>90</sup> Pure crystalline phosphorus tri-iodide,

<sup>84</sup> K. A. Hofmann and U. Hofmann, *Ber.*, 1926, **59**, [B], 2574; **A.**, 1927, 31.

<sup>85</sup> H. Reihlen and A. Hake, *Annalen*, 1927, **452**, 47; **A.**, 219.

<sup>86</sup> W. F. Busse and F. Daniels, *J. Amer. Chem. Soc.*, 1927, **49**, 1257; **A.**, 635; compare R. G. W. Norrish, *Nature*, 1927, **119**, 123; **A.**, 119.

<sup>87</sup> P. Askenasy, E. Elöd, and H. Zieler, *Z. anorg. Chem.*, 1927, **162**, 161; **A.**, 635.

<sup>88</sup> S. A. Vosnessenski, *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 221; **A.**, 741.

<sup>89</sup> E. J. Bowen and E. G. Pells, *J.*, 1927, 1096; **A.**, 633.

<sup>90</sup> W. F. Busse, *Ann. Physik*, 1927, [iv], **82**, 873; **A.**, 633.

m. p.  $61.0^{\circ}$ , and di-iodide, m. p.  $124.5^{\circ}$ , have been prepared.<sup>91</sup> Besson's supposed suboxide,  $P_2O$ , has been shown to be a mixture of finely divided amorphous phosphorus with adsorbed phosphorous acid.<sup>92</sup> It has been shown that a variable mixture of phosphorus sulphides is formed when phosphine is heated with sulphur or with hydrogen sulphide.<sup>93</sup>

The glow of arsenic in air or oxygen, which appears suddenly at temperatures between  $250^{\circ}$  and  $310^{\circ}$  when the pressure is reduced below a critical value, differs from that of phosphorus, since it is not affected by small quantities of carbon tetrachloride, nitrobenzene, or sulphur dioxide. The appearance of the glow is favoured by a rapid removal of the arsenic trioxide formed in the reaction, and it is suggested that the velocity of removal of the product by evaporation and condensation is the determining factor in the formation of the glow.<sup>94</sup>

An extensive research is reported on the oxides of antimony, and a new oxide,  $Sb_6O_{13}$ , is described which is very stable and may be heated for a long period at  $800^{\circ}$  without decomposition; once decomposition has begun, however, it proceeds rapidly at lower temperatures. The paper contains much thermal and vapour-pressure data which cannot be summarised here.<sup>95</sup>

Investigations of tervalent vanadium<sup>96</sup> and of the action of hydrogen peroxide on acidified solutions of vanadic acid have been made.<sup>97</sup>

#### Group VI.

The fact that the density of solid oxygen at  $-252^{\circ}$  is 0.034 unit greater than the accepted value (*viz.*, 1.46) affords additional evidence of the existence of a second, denser form of solid oxygen stable at temperatures much lower than the melting point. The existence of two forms of oxygen accords with the properties of other members of the same group.<sup>98</sup>

When mixtures of sulphur and chlorine are heated at  $100^{\circ}$  in sealed tubes, or with the addition of a trace of iodine as catalyst, the product gives a freezing-point curve showing, in addition to the familiar maxima due to the crystallisation of  $S_2Cl_2$  and  $SCl_4$ , two well-defined breaks which are attributed to the crystallisation of

<sup>91</sup> F. E. E. Germann and R. N. Traxler, *J. Amer. Chem. Soc.*, 1927, **49**, 307; **A.**, 328.

<sup>92</sup> L. J. Chalk and J. R. Partington, *J.*, 1927, 1930; **A.**, 950.

<sup>93</sup> L. Delachaux, *Helv. Chim. Acta*, 1927, **10**, 195; **A.**, 326.

<sup>94</sup> H. J. Emeléus, *J.*, 1927, 783; **A.**, 497.

<sup>95</sup> A. Simon and E. Thaler, *Z. anorg. Chem.*, 1927, **162**, 253; **A.**, 730.

<sup>96</sup> J. Meyer and E. Markowicz, *ibid.*, 1926, **157**, 211; **A.**, 1927, 32.

<sup>97</sup> J. Meyer and A. Pawletta, *Z. physikal. Chem.*, 1927, **125**, 49; **A.**, 326.

<sup>98</sup> J. C. McLennan and J. O. Wilhelm, *Phil. Mag.*, 1927, [vii], **3**, 383; **A.**, 297.



$\text{SCl}_2$  and  $\text{S}_3\text{Cl}_4$ . Freshly prepared mixtures of sulphur monochloride with an equilibrium mixture containing about 70% of chlorine exhibit a maximum freezing point at the composition  $\text{SCl}_2$ , and a solid of this composition is obtained on freezing.<sup>99</sup>

It has been shown that the burning of sulphur vapour in oxygen gives rise to sulphur trioxide; this is formed by direct union and not by a secondary oxidation of sulphur dioxide.<sup>1</sup>

The molecular weights of the various forms of sulphur trioxide have been determined in various solvents and by measurements of vapour density.<sup>2</sup> Because negative catalysts such as sulphur, tellurium, carbon tetrachloride, and phosphorus oxychloride stabilise the  $\alpha$ -form of sulphur trioxide, it is suggested that it has the structure  $\text{S}(\text{:O})_3$ , whilst the  $\beta$ -form, disulphuric anhydride, has the constitution  $\text{O} \begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{S} < \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix} > \text{S} \begin{smallmatrix} \nwarrow \\ \nearrow \end{smallmatrix} \text{O}$ .<sup>3</sup>

A long and very important paper has appeared on the interrelationships of the sulphur acids; it contains so much valuable detail that it cannot usefully be summarised here, and the reader is referred to the original communication. A new anhydro-acid,  $\text{H}_2\text{S}_4\text{O}_5$ , is described which is oxidised by methylene-blue to tetrathionic acid. The acid results from one of the three possible modes of decomposition of thiosulphuric acid:  $\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{SO}_3 + \text{S}$ ;  $2\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{S} + \text{H}_2\text{S}_3\text{O}_6$ ;  $2\text{H}_2\text{S}_2\text{O}_3 \rightleftharpoons \text{H}_2\text{O} + \text{H}_2\text{S}_4\text{O}_5$ .<sup>4</sup>

Sulphur trioxide readily reacts with nitric oxide at  $60^\circ$ , yielding the product  $2\text{SO}_3\cdot\text{NO}$ , m. p.  $215\text{--}220^\circ$  after darkening and softening at  $180^\circ$ , b. p.  $275^\circ/715\text{ mm.}$  The substance is readily decomposed by water into sulphuric acid and nitric oxide, but does not react with ferrous sulphate or cupric sulphate dissolved in concentrated sulphuric acid. When heated, it decomposes into sulphur dioxide and nitrogen peroxide, from which it may be prepared at  $200\text{--}300^\circ$ . If, however, the gases are moist, nitrosylsulphuric acid is formed in which drops of "blue acid" appear after some time. The "acid" is regarded as an oxide of nitrogen intermediate between  $\text{NO}_{1.5}$  and  $\text{NO}$ . Raschig's conception that "blue acid" has the composition  $\text{H}_2\text{SNO}_5$  is rendered improbable by the observation that its absorption spectrum does not resemble those of the compounds  $\text{CuSO}_4\cdot\text{NO}$  and  $\text{FeSO}_4\cdot\text{NO}$ .<sup>5</sup>

<sup>99</sup> T. M. Lowry, L. P. McHatton, and G. G. Jones, *J.*, 1927, 746; **A.**, 505.

<sup>1</sup> J. Cornog, W. Dargan, and P. Bender, *J. Amer. Chem. Soc.*, 1926, **48**, 2757; **A.**, 1927, 32.

<sup>2</sup> G. Oddo and A. Casalino, *Gazzetta*, 1927, **57**, 60, 75; G. Oddo, *ibid.*, pp. 29, 104; **A.**, 312, 300, 432.

<sup>3</sup> G. Oddo and A. Sconzo, *ibid.*, p. 83; **A.**, 432.

<sup>4</sup> H. Bassett and R. G. Durrant, *J.*, 1927, 1401; **A.**, 843.

<sup>5</sup> W. Manchot [with J. König and S. Reimlinger], *Ber.*, 1926, **59**, [B], 2672; **A.**, 1927, 32.

If the solution, obtained by the action of carbon monoxide on magnesium ethyl in the presence of chromic chloride is hydrolysed with sulphuric acid at  $0^\circ$ , and the ethereal layer is separated, neutralised, dried, and evaporated, crystals of chromium carbonyl,  $\text{Cr}(\text{CO})_6$ , separate. The pure carbonyl has  $d^{18}_4$  1.77, is slightly soluble in benzene and ether, but more soluble (2%) in chloroform and carbon tetrachloride, decomposes rapidly into chromic oxide at  $210^\circ$ , melts in a sealed tube at  $149\text{--}150^\circ$ , and irreversibly deposits a chromium mirror at  $230^\circ$ . The carbonyl is unattacked by dilute acids, bromine, and iodine; fuming nitric acid converts it into chromic nitrate and free carbon.<sup>6</sup>

Molybdenyl monochloride,  $\text{MoOCl}_2 \cdot 4\text{H}_2\text{O}$ , has been shown to exist in two stereoisomeric forms,<sup>7</sup> and the behaviour of the other molybdenyl salts has suggested that in certain circumstances oxygen may occupy two positions in the co-ordination sphere.<sup>8</sup> A large number of hydrated molybdotungstates have been prepared and analysed.<sup>9</sup>

Selenium oxyfluoride and tetrafluoride, both colourless, fuming liquids, have been prepared, and there is some evidence that a lower fluoride,  $\text{Se}_2\text{F}_2$ , may exist.<sup>10</sup> Attempts to repeat the production of selenium trioxide previously reported<sup>11</sup> have been unsuccessful.<sup>12</sup>

### Group VII.

The oxidising action of fluorine on water, alkali hydroxide, sulphuric acid, phosphoric acid, phosphates, carbonates, and borates gives highly oxygenated compounds of the peroxide, peracid, or ozonide type in most cases.<sup>13</sup> Passage of fluorine into a fairly concentrated solution of cobaltous sulphate in sulphuric acid yields cobaltic sulphate, which is extremely unstable: the cobaltic salt is formed only with difficulty in dilute solutions.<sup>14</sup>

A gaseous, oxygen compound of fluorine is produced when water is present in the electrolysis of molten acid potassium fluoride below  $100^\circ$ . The gas has not been prepared in the pure state, but studies of its mixtures with oxygen point to the formula  $\text{F}_2\text{O}$ . Such mixtures

<sup>6</sup> A. Job and A. Cassal, *Bull. Soc. chim.*, 1927, [iv], **41**, 1041; **A.**, 1044.

<sup>7</sup> W. Wardlaw and R. L. Wormell, *J.*, 1927, 130; **A.**, 296.

<sup>8</sup> *Idem*, *ibid.*, p. 1087; **A.**, 636.

<sup>9</sup> L. Fernandes, *Gazzetta*, 1926, **56**, 655; **A.**, 1927, 33.

<sup>10</sup> E. B. R. Prideaux and C. B. Cox, *J.*, 1927, 928; **A.**, 532.

<sup>11</sup> *Ann. Reports*, 1923, **20**, 52.

<sup>12</sup> J. Meyer and A. Pawletta, *Ber.*, 1927, **60**, [B], 985; **A.**, 532.

<sup>13</sup> F. Fichter and W. Bladergroen, *Helv. Chim. Acta*, 1927, **10**, 549, 553, 559, 566; **A.**, 741.

<sup>14</sup> F. Fichter and H. Wolfmann, *Helv. Chim. Acta*, 1926, **9**, 1093; **A.**, 1927, 123.

have the odour of fluorine, do not act on glass even at high temperatures, are stable in the presence of water, but liberate iodine from potassium iodide.<sup>15</sup>

A compound,  $K_2Mn(CN)_3$ , containing univalent manganese, has been produced by the reduction of potassium manganocyanide by aluminium filings or Devarda's alloy; it has very strong reducing properties.<sup>16</sup>

### Group VIII.

A number of salts have been described in which cobalt and nickel are believed to be univalent,<sup>17</sup> and a description has been given of the preparation and properties of certain perferrates. Potassium perferrate is more stable than potassium ferrate and can be purified by cautious sublimation.<sup>18</sup>

The passivity of iron has been shown to be due to the existence of a protective film which is too thin to give interference tints. This film, which consists of ferric oxide or hydroxide, has been obtained as a transparent envelope by dissolving the metal beneath by anodic treatment in sodium chloride solutions. The transparent skin can also be removed by treatment with iodine. Chlorides favour the activation, since the film is permeable to chloride ions, and under anodic conditions the metal is dissolved away beneath the skin; mere immersion in a chloride solution, under conditions precluding the flow of local currents, does not cause activation. The attack on passive iron is often localised at the water surface, the protective film tending to cling to the gas-liquid rather than to the metal-liquid interface, thus initiating a breakdown. Nitric acid is a rather untrustworthy reagent for producing passivity. Transparent films have also been isolated from the surface of passive copper and aluminium.<sup>19</sup>

Differences of density and viscosity in a series of aqueous solutions of cobalt chloride and hydrochloric acid show when plotted a well-marked inflexion and maximum respectively, which are considered to mark the concentration of acid at which equal numbers of the blue and the red ions are present. This point does not correspond to the maximum colour change because the blue of  $CoCl_4''$  is more intense than the red of  $Co(H_2O)_6^{++}$ .<sup>20</sup> Other workers prefer to

<sup>15</sup> P. Lebeau and A. Damiens, *Compt. rend.*, 1927, **185**, 652; **A.**, 1044.

<sup>16</sup> W. Manchot and H. Gall, *Ber.*, 1927, **60**, [B], 191; **A.**, 220.

<sup>17</sup> W. Manchot, *ibid.*, 1926, **59**, [B], 2445; **A.**, 1927, 33; G. Grube [with H. Lieder and P. Schächterle], *Z. Elektrochem.*, 1926, **32**, 561; **A.**, 1927, 119.

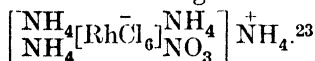
<sup>18</sup> D. K. Goralevitch, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1129; **A.**, 1927, 433.

<sup>19</sup> U. R. Evans, *J.*, 1927, 1020; **A.**, 619.

<sup>20</sup> O. R. Howell, *J.*, 1927, 158; **A.**, 205.

explain the change in terms of complex formation, and compounds of the type  $\text{CoCl}_2 \cdot \text{H}_2\text{O}$  (blue or violet),  $\text{CoCl}_2 \cdot 4\text{H}_2\text{O}$  (red), and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (rose) are postulated.<sup>21</sup>

Ruthenium dichloride and dibromide have been produced by reducing the tri-halogen salts with hydrogen in suitable organic solvents in the presence of catalysts, and their properties have been further described.<sup>22</sup> The structure of Wilm's rhodium chloronitrate has been investigated and the following formula has been suggested:



### *Systems.*

A great deal of work has been done on various types of systems which it is impossible to describe in this Report. It may be useful, however, to give here the titles, in the order in which they appear in the Abstracts.

Potassium zincicyanide–potassium mercuricyanide–potassium nickelocyanide–potassium cadmicyanide<sup>24</sup>; mercuric chloride–silver iodide<sup>25</sup>; lanthanum sulphate–ammonium sulphate–water<sup>26</sup>; beryllium chloride–chloride of lead or silver or cadmium<sup>27</sup>; sodium nitrate–sodium chloride–water<sup>28</sup>; sodium oxide–nitrogen pentoxide–water<sup>29</sup>; sodium, or potassium, or rubidium or caesium chloride–cobaltous chloride–water<sup>30</sup>; magnesium sulphate–zinc sulphate<sup>31</sup>; lithium chloride or bromide–water<sup>32</sup>; zinc hydroxide–zinc oxide–sodium zincate–sodium hydroxide<sup>33</sup>; lithium chlorate–water<sup>34</sup>;

<sup>21</sup> A. Hantzsch, *Z. anorg. Chem.*, 1927, **159**, 273; **A.**, 205; compare J. Gröb and R. Schmid, *ibid.*, **162**, 321; **A.**, 728; A. Hantzsch, *ibid.*, **166**, 237; **A.**, 1023.

<sup>22</sup> H. Gall and G. Lehmann, *Ber.*, 1926, **59**, [B], 2856; **A.**, 1927, 123.

<sup>23</sup> O. E. Zwiagincev, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 170; **A.**, 1927, 123.

<sup>24</sup> A. S. Corbet, *J.*, 1926, 3190; **A.**, 1927, 112.

<sup>25</sup> A. G. Bergman and T. A. Henke, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 80; **A.**, 1927, 112.

<sup>26</sup> F. Zambonini and (Miss) A. Stolfi, *Atti R. Accad. Lincei*, 1926, [vi], **4**, 424; **A.**, 1927, 112.

<sup>27</sup> J. M. Schmidt, *Bull. Soc. chim.*, 1926, [iv], **39**, 1686; **A.**, 1927, 112.

<sup>28</sup> F. Hölzl and H. Crotogino, *Z. anorg. Chem.*, 1926, **159**, 78; **A.**, 1927, 207.

<sup>29</sup> W. T. Nikolaiev, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 557; **A.**, 1927, 313.

<sup>30</sup> H. W. Foote, *Amer. J. Sci.*, 1927, **13**, 158; **A.**, 313.

<sup>31</sup> H. G. K. Westenbrink, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1374; **A.**, 1927, 417.

<sup>32</sup> G. F. Hüttig and W. Steudemann, *Z. physikal. Chem.*, 1927, **126**, 105; **A.**, 517.

<sup>33</sup> E. Müller, J. Müller, and A. Fauvel, *Z. Elektrochem.*, 1927, **33**, 134; **A.**, 518.

<sup>34</sup> C. A. Kraus and W. M. Burgess, *J. Amer. Chem. Soc.*, 1927, **49**, 1226; **A.**, 627.

carbon disulphide-hydrogen sulphide<sup>35</sup>; manganese-zinc<sup>36</sup>; calcium ferrocyanide-sodium ferrocyanide-water<sup>37</sup>; barium iodide-iodine-water<sup>38</sup>; sodium chloride-potassium chlorate-sodium chlorate-potassium chloride<sup>39</sup>; potassium oxide-ammonia-phosphorus pentoxide-water<sup>40</sup>; cobalt chloride-rubidium or lithium or zinc or cadmium chloride-water<sup>41</sup>; uranyl sulphate-ammonium or potassium or sodium sulphate-water<sup>42</sup>; copper-aluminium-manganese<sup>43</sup>; iron-silicon<sup>44</sup>; iron-cobalt-nickel<sup>45</sup>; neodymium sulphate-rubidium sulphate-water<sup>46</sup>; silver nitrate-lithium or rubidium nitrate<sup>47</sup>; neodymium sulphate-ammonium sulphate<sup>48</sup>; cerium sulphate-sodium sulphate<sup>49</sup>; aluminium nitrate-water<sup>50</sup>; sodium or lithium chloride-lead chloride-water<sup>51</sup>; boron trioxide-sulphur trioxide or phosphorus pentoxide-water.<sup>52</sup>

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<sup>35</sup> W. Biltz and M. Bräutigam, *Z. anorg. Chem.*, 1927, **162**, 49; **A.**, 627.

<sup>36</sup> C. L. Ackermann, *Z. Metallk.*, 1927, **19**, 200; **A.**, 627.

<sup>37</sup> (Miss) M. Farrow, *J.*, 1927, 1153; **A.**, 628.

<sup>38</sup> A. C. D. Rivett and J. Packer, *ibid.*, p. 1342; **A.**, 731.

<sup>39</sup> C. Di Capua and U. Scaletti, *Gazzetta*, 1927, **57**, 391; **A.**, 731.

<sup>40</sup> E. Jänecke, *Z. physikal. Chem.*, 1927, **127**, 71; **A.**, 731.

<sup>41</sup> A. Bonrath, *Z. anorg. Chem.*, 1927, **163**, 396; **A.**, 829.

<sup>42</sup> A. Colani, *Compt. rend.*, 1927, **185**, 273; **A.**, 830.

<sup>43</sup> W. Krings and W. Ostmann, *Z. anorg. Chem.*, 1927, **163**, 145; **A.**, 830.

<sup>44</sup> T. Murakami, *Sci. Rep. Tôhoku Imp. Univ.*, 1927, **16**, 475; **A.**, 830.

<sup>45</sup> T. Kasé, *ibid.*, p. 491; **A.**, 830.

<sup>46</sup> F. Zambonini and V. Caglioti, *Atti R. Accad. Lincei*, 1927, [vi], **5**, 630; **A.**, 842.

<sup>47</sup> A. P. Palkin, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1334; **A.**, 1927, 939.

<sup>48</sup> F. Zambonini and A. Stolfi, *Atti R. Accad. Lincei*, 1927, [vi], **5**, 832; **A.**, 949.

<sup>49</sup> F. Zambonini and S. Restaino, *ibid.*, p. 828; **A.**, 949.

<sup>50</sup> G. Malquori, *ibid.*, p. 892; **A.**, 949.

<sup>51</sup> G. E. R. Deacon, *J.*, 1927, 2063; **A.**, 1030.

<sup>52</sup> M. Levi and L. F. Gilbert, *ibid.*, p. 2117; **A.**, 1030.

## ORGANIC CHEMISTRY.

### PART I.—ALIPHATIC DIVISION.

#### *Alcohols, Aldehydes, and Ketones.*

THE action of fused alkali hydroxides at 250—300° upon ethyl alcohol is slow and several reactions appear to take place simultaneously, sodium carbonate, oxalate and acetate, hydrogen, methane, and ethylene being produced. Acetaldehyde under similar conditions at 250° reacts to the extent of 90% in accordance with the equation  $\text{C}_2\text{H}_4\text{O} + \text{NaOH} \longrightarrow \text{NaOAc} + \text{H}_2$ . Higher temperatures promote the formation of methane and sodium carbonate:  $\text{C}_2\text{H}_4\text{O} + 2\text{NaOH} \longrightarrow \text{H}_2 + \text{CH}_4 + \text{Na}_2\text{CO}_3$ . Acetone was found to behave like acetaldehyde.<sup>1</sup>

Several communications have appeared dealing with the structure of the acetylenic  $\gamma$ -glycols. In one of these <sup>2</sup> a study is made of the physical properties and reactions of  $\beta\epsilon$ -dibromo- $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene and of the product resulting from the action of phosphorus tribromide on  $\beta\epsilon$ -dimethyl- $\Delta\gamma$ -hexinene- $\beta\epsilon$ -diol. The crystalline dibromide, m. p. 39°, previously obtained by G. Dupont,<sup>3</sup> is comparatively inert and appears to possess the ethylenic structure  $\text{CMe}_2\text{:CBr}\cdot\text{CBr}\cdot\text{CMe}_2$  and not Dupont's acetylenic structure. The glycol on treatment with phosphorus tribromide gives a mixture of products, amongst which is a less stable isomeric dibromide, m. p. 46—48°, which probably possesses the acetylenic formula



and passes easily into the ethylenic isomeride. Other varieties are present, however, and the reaction is apparently complex. These conclusions are in essential agreement with the results obtained in another investigation of the same problem,<sup>4</sup> with the exception that in the latter case the acetylenic dibromide, m. p. 46—48°, was found to be comparatively inert. The action of hydriodic acid on the glycol effects conversion into a crystalline di-iodide,  $\text{C}_8\text{H}_{14}\text{I}_2$ ,

<sup>1</sup> H. S. Fry and E. L. Schulze, *J. Amer. Chem. Soc.*, 1926, **48**, 958; *A.*, 1926, 710.

<sup>2</sup> W. N. Krestinski, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1067; *A.*, 1927, 442. See also *Ber.*, 1926, **59**, [B], 1930; *A.*, 1926, 1121.

<sup>3</sup> *Compt. rend.*, 1911, **152**, 197; *A.*, 1911, i, 173.

<sup>4</sup> J. S. Salkind and M. P. Sigova, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1039; *A.*, 1927, 442.

m. p. 75°, analogous in structure to the ethylenic dibromide,<sup>5</sup> and the investigation has been extended to include the action of hydrobromic acid on one of the stereoisomerides of  $\alpha\delta$ -diphenyl- $\Delta^{\beta}$ -butinene- $\alpha\delta$ -diol.<sup>6</sup> This gives a complex mixture of products, amongst which are two solid dibromides, a solid tribromide, a liquid dibromide and a liquid monobromide. A detailed study of the properties of each of these shows that the monobromide, for which the formula  $\begin{array}{c} \text{CH}-\text{CHPh} \\ | \\ \text{CBr}-\text{CHPh} \end{array} > \text{O}$  is suggested, yields no di-

bromide on further bromination, and the dibromides must therefore be formed by means of an independent parallel reaction. To the dibromide, m. p. 114—115°, the structure  $\text{CHPh}:\text{CBr}:\text{CH}:\text{CPhBr}$  is ascribed, and the isomeric dibromide, m. p. 92—95°, may be either  $\text{CHPhBr}:\text{C}:\text{C}:\text{CHPhBr}$  or  $\text{CPhBr}:\text{CH}:\text{CH}:\text{CPhBr}$ .

Oleyl alcohol (*n-trans*- $\Delta^7$ -octadecen- $\alpha$ -ol) has been converted *via* the liquid bromine additive compound, which is then treated with silver acetate in acetic acid, into the diacetate of oleicerin (*n-trans*-octadecane- $\alpha\kappa$ -triol). The free triol obtained on hydrolysis is a solid, m. p. 126.5°. The corresponding *n-cis*-octadecane- $\alpha\kappa$ -triol (elaidicerin, m. p. 92°) may be prepared in a similar way from elaidyl alcohol.<sup>7</sup>

A further addition to the number of organic compounds containing fluorine has been made by the preparation of trifluorotert.-butyl alcohol from *iso*amyl trifluoroacetate by reaction with magnesium methyl iodide, the fluorine remaining unattacked. The alcohol (m. p. 20.8°) may be converted by treatment with phosphorus pentabromide, but not with concentrated sulphuric acid, into  $\gamma\gamma\gamma$ -trifluoroisobutylene, which combines without loss of fluorine with hydrogen bromide and with bromine.<sup>8</sup>

A study of the absorption curves in ultra-violet light of acetaldehyde and paracetaldehyde solutions indicates the presence of an enolic form of the aldehyde, the proportion being 1 in 335 for acetaldehyde in sodium hydroxide, 1 in 830 in hydrochloric acid, and 1 in 1045 for paracetaldehyde in hydrochloric acid.<sup>9</sup>

The enolisation of acetone has been investigated by means of the compound  $(\text{CH}_2:\text{CMe}:\text{O})_2\text{Hg}\cdot 2\text{HgO}$  obtained from freshly precipitated mercuric oxide and acetone in the presence of potassium hydroxide. It appears that the enolisation of acetone is analogous

<sup>5</sup> J. S. Salkind, B. Rubin, and A. Kruglov, *ibid.*, p. 1044; **A.**, 442.

<sup>6</sup> J. S. Salkind and A. Kruglov, *ibid.*, p. 1052; **A.**, 443; *Ber.*, 1926, **59**, 1936; **A.**, 1926, 1121.

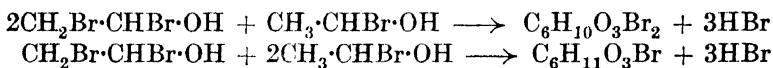
<sup>7</sup> E. André and (Mlle.) T. François, *Compt. rend.*, 1927, **185**, 387; **A.**, 957.

<sup>8</sup> F. Swarts, *Bull. Soc. chim. Belg.*, 1927, **36**, 191; **A.**, 442.

<sup>9</sup> S. A. Schoù, *Compt. rend.*, 1927, **184**, 1452; **A.**, 751.

to that of ethyl acetoacetate, a maximum amount of the enolic modification being formed in the presence of 0.037*M*-alkali, further increase in the alkali concentration being without effect.<sup>10</sup>

The action of bromine (1 mol.) on paracetaldehyde at low temperatures gives bromoparacetaldehyde, m. p. 27.5°, together with the dibromo-compound. The former decomposes when heated at 130° into bromoacetaldehyde. The reaction between bromine (3 mols.) and paracetaldehyde is complicated by the action of hydrogen bromide on the aldehyde, which leads to the formation of tetrabromobutaldehyde. In all these changes very slight evolution of hydrogen bromide occurs and the mechanism of the reaction is said to depend on an equilibrium between paracetaldehyde and acetaldehyde, the latter of which becomes enolised under the influence of bromine to give vinyl alcohol. The very unstable αβ-dibromoethyl alcohol is then formed, which passes into tribromoparacetaldehyde and hydrogen bromide. The liberated acid may combine with acetaldehyde or vinyl alcohol, yielding α-bromoethyl alcohol, which with αβ-dibromoethyl alcohol gives a mixture of mono- and di-bromoparacetaldehyde<sup>11</sup> in accordance with the two equations :



Bromination of polymerised aldehydes at low temperatures has been employed as a means of obtaining α-hydroxy-aldehydes. Thus parapropaldehyde with bromine (1 mol.) at -10°, followed by treatment with alcohol, gives the acetal of α-bromopropaldehyde, which when hydrolysed with water yields α-hydroxypropaldehyde. Similarly from the acetals of αα-dibromopropaldehyde and α-bromoheptaldehyde, pyruvaldehyde and a dimeric form of α-hydroxyheptaldehyde were obtained.<sup>12</sup> A study of the complex reaction between magnesium ethyl bromide and α-bromo-aldehydes reveals a certain similarity in behaviour between the latter compounds and acyl halides. For instance, α-bromoheptaldehyde and magnesium methyl bromide give a very small amount of γ-bromo-β-octanol, together with methyl hexyl ketone, a tertiary alcohol (probably β-methyloctan-β-ol), and an olefine, C<sub>9</sub>H<sub>18</sub>, which results from dehydration of the tertiary alcohol. Lead hydroxide and α-bromoheptaldehyde give heptoic acid in place of the expected

<sup>10</sup> W. L. Evans and W. D. Nicoll, *J. Amer. Chem. Soc.*, 1925, **47**, 2789; *A.*, 1926, 51.

<sup>11</sup> A. Stepanov, N. Preobraschenski, and M. Sehtschukina, *Ber.*, 1926, **59**, 2533; *A.*, 1927, 42. Compare also R. Dworzak, *Monatsh.*, 1925, **46**, 253; *A.*, 1926, 385.

<sup>12</sup> R. Dworzak and P. Pffferling, *Monatsh.*, 1927, **48**, 251; *A.*, 1055.



aldehyde-alcohol, and it is thus probable that the methyl hexyl ketone is formed by molecular transformation during the action with the magnesium methyl bromide, the reaction thereafter resembling that with an acyl halide.<sup>13</sup>

The chemical properties of glyceraldehyde and of dihydroxyacetone are of special interest in view of the importance of these compounds both in physiological processes and as simple hydroxy-compounds related to the aldoses and ketoses. A. Wohl's method<sup>14</sup> of preparing glyceraldehyde has been improved and a detailed examination of the *dl*-compound has been commenced.<sup>15</sup> During the isolation of *dl*-glyceraldehyde from its diethylacetal a viscous opaque syrup can be obtained which possesses unexpected properties. It is definitely enolic in character, and is unimolecular in aqueous solution, whereas the crystalline variety is bimolecular and in aqueous solution contains only a trace of the enolic modification. The enol appears to be present also in an alkaline solution of crystalline glyceraldehyde and, since this enol is identical with the enolic modification of dihydroxyacetone, an explanation readily follows of the mechanism of acrose formation from glyceraldehyde, the essential reaction being the aldol condensation of glyceraldehyde and dihydroxyacetone. The transformation of bimolecular glyceraldehyde into dihydroxyacetone in yields up to 49% has been effected by treatment with boiling pyridine<sup>16</sup> and on the basis of this and other evidence, such as the indifference of the acetate towards phenylhydrazine and the non-formation of an isopropylidene ether, the formula  $\left( \text{O} < \begin{array}{c} \text{CH} \cdot \text{OH} \\ \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{array} \right)_2$  is suggested. The diethylacetal of glyceraldehyde, on the other hand, reacts readily with acetone to form the isopropylidene ether.

The action of hydrobromic acid in acetic acid on diacetylglyceraldehyde gives the bimolecular acetobromoglyceraldehyde, m. p. 168—169°, to which the formula  $\left( \text{O} < \begin{array}{c} \text{CHBr} \\ \text{CH} \cdot \text{CH}_2 \cdot \text{OAc} \end{array} \right)_2$  is ascribed. Methyl alcohol and silver carbonate give the corresponding acetylated methylcycloacetal, from which bimolecular glyceraldehyde methylcycloacetal, m. p. 158.5—159.5°, may be obtained by the action of ammonia in methyl alcohol,  $\left( \text{O} < \begin{array}{c} \text{CH} \cdot \text{OMe} \\ \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \end{array} \right)_2$ . The very close resemblance between these reactions and the corresponding properties of acetobromoglucose is further shown by the

<sup>13</sup> A. Kirmann, *Compt. rend.*, 1927, **184**, 1463; *A.*, 751.

<sup>14</sup> *Ber.*, 1898, **31**, 1796, 2394; *A.*, 1898, i, 555; 1899, i, 11.

<sup>15</sup> H. G. Reeves, *J.*, 1927, 2478; *A.*, 1172.

<sup>16</sup> H. O. L. Fischer, C. Taube, and E. Baer, *Ber.*, 1927, **60**, 479; *A.*, 340.

transformation of acetobromoglyceraldehyde to bimolecular acetyl-glyceraldehyde, m. p.  $118.5^{\circ}$ . Some similar bimolecular compounds have been obtained from glycollaldehyde (*e.g.*, glycollaldehyde methylcycloacetal, m. p.  $72^{\circ}$ ), and from dihydroxyacetone, which gives the methylcycloacetal  $\left[ \text{O} < \overset{\text{CH}_2}{\underset{\text{C}(\text{OMe})}{\text{C}}} \cdot \text{CH}_2 \cdot \text{OH} \right]_2$ , m. p.  $131-132^{\circ}$ .<sup>17</sup>

The elucidation of the particular type of polymerisation found in the dimeric compounds may be expected to yield results of importance both for this and for other fields of investigation.

A convenient method for the preparation of isopropylidene ethers depends on the use of anhydrous zinc chloride as condensing agent in dry acetone solution.<sup>18</sup> The ethers thus prepared are more stable than those obtained by the aid of acids, and of the many substances treated by this method only *d*-glucose showed an abnormal behaviour. The process is specially valuable as a means of isolating dihydroxyacetone.

A general method for the preparation of ketone-alcohols of the type  $\text{CHPh}(\text{OH}) \cdot \text{COR}$  is that of acting on phenylglycollamide or the corresponding nitrile with magnesium alkyl halides. Secondary alcohols of the type  $\text{CHPhR} \cdot \text{OH}$  are, however, always formed as by-products in the case of the nitrile.<sup>19</sup> The preparation of the ketone-alcohols  $\text{CHPh}(\text{OH}) \cdot \text{COR}$ , in which  $\text{R} = \text{ethyl, propyl, isopropyl, } n\text{-butyl, isobutyl, and benzyl}$ , is described. It has been found that  $\alpha$ -keto-alcohols, when heated in alcoholic solution at  $120-130^{\circ}$  with a small quantity of sulphuric acid, undergo molecular rearrangement. The carbonyl group moves so as to take up a position as near as possible to the end of the chain, the tendency being for the formation of an acetyl group. Thus butyrylethylcarbinol is transformed into propionylpropylcarbinol. The suggestion is made that a similar transformation may play a part in the course of alcoholic fermentation.<sup>20</sup>

A detailed criticism has been contributed of the formula  $\text{CH}_2(\text{OH}) \cdot \text{O} \cdot \text{SO}_2\text{Na}$  assigned by E. Knoevenagel<sup>21</sup> to the sodium hydrogen sulphite addition compound of formaldehyde. The stability of the addition compound towards oxidising agents, its ready reducibility, and its reaction with phenols to give sulphonic acids are all incompatible with the above formula and evidence of the direct attachment of sulphur to carbon is provided. Ammonia

<sup>17</sup> H. O. L. Fischer and C. Taube, *Ber.*, 1927, **60**, 1704; **A.**, 857.

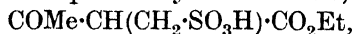
<sup>18</sup> *Idem, ibid.*, p. 485; **A.**, 338.

<sup>19</sup> M. Tiffeneau and (Mlle.) J. Levy, *Bull. Soc. chim.*, 1925, **37**, 1247; **A.**, 1926, 71.

<sup>20</sup> A. Favorski, *ibid.*, 1926, **39**, 216; **A.**, 1926, 500.

<sup>21</sup> *Ber.*, 1904, **37**, 4060; **A.**, 1904, i, 1027.

reacts with formaldehyde hydrogen sulphite to give a compound whose properties show it to be aminomethanesulphonic acid and furthermore formaldehyde bisulphite and ethyl acetoacetate may be made to yield ethyl  $\alpha$ -sulphomethylacetoacetate,



which is hydrolysed in alkaline solution to  $\beta$ -sulphopropionic acid and in acid solution to  $\gamma$ -ketobutanesulphonic acid. It is shown that the change is not explicable on the grounds of initial fission of the aldehyde bisulphite with the addition of sulphurous acid at a later stage. The attachment of both hydroxy- (or amino-) and sulphonic groups to the same carbon atom confers a special lability on each, which is responsible, in addition to other reactions, for the ready loss of the latter group as sulphur dioxide. In the second of the two papers referred to, a wealth of experimental evidence is cited to support the formulation of formaldehyde bisulphite as sodium hydroxymethanesulphonate,  $\text{CH}_2(\text{OH})\cdot\text{SO}_3\text{Na}$ .<sup>22</sup>

#### *Carbohydrates.*

*Monosaccharides, Lactones, and Glucosides.*—The revision of the structural formulæ of the most commonly occurring forms of glucose, reported last year, has received wide acceptance, and the generalisation which accompanied this revision has passed into common use in the formulations applied to the carbohydrate group. Confirmatory evidence of the nature of the oxide rings in derivatives of the normal and also of the labile or  $\gamma$ -sugars has been furnished from many sides, and this evidence has now assumed so convincing a character as to place the issue beyond any reasonable doubt. There is still need for reform in the nomenclature adopted to define the structural relationships of the sugars, and a paragraph on this problem at the end of the present sub-section reports on some recent suggestions.

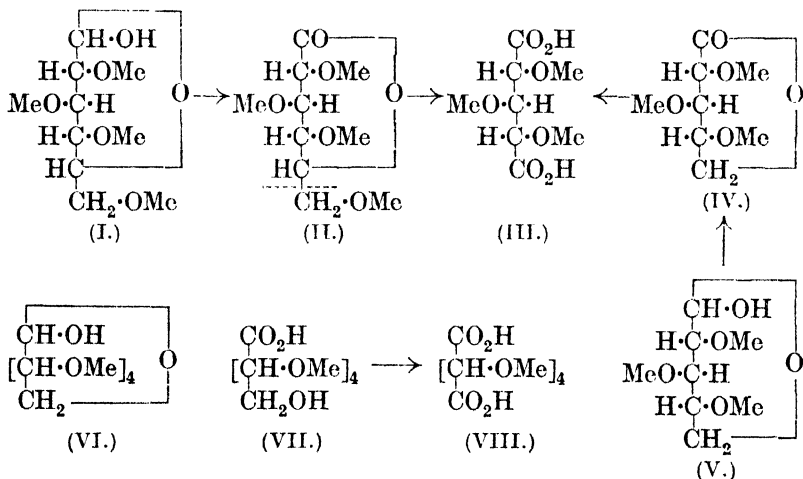
A comparative study of ten methylated lactones derived from simple sugars has shown that the rate of hydrolysis of five lactones obtained from normal sugars is many times greater than in the case of the remaining five lactones, which are related to the  $\gamma$ -sugars.<sup>23</sup> The curves showing the change  $\text{lactone} \rightleftharpoons \text{acid}$  reveal well-marked differences in the stability of the lactones as between the two types. Those derived from normal sugars are seen to be  $\delta$ -lactones having six-membered rings, whereas those related to  $\gamma$ -sugars are  $\gamma$ -lactones having five-membered rings. Six of the series of ten lactones are

<sup>22</sup> F. Raschig, *Ber.*, 1926, **59**, 859; *A.*, 1926, 599; F. Raschig and W. Prahl, *Annalen*, 1926, **448**, 265; *A.*, 1926, 939.

<sup>23</sup> H. D. K. Drew, E. H. Goodyear, and W. N. Haworth, *J.*, 1927, 1237; *A.*, 750.

crystalline and others give characteristic phenylhydrazides which are crystalline. It is possible to diagnose by these methods which member of a pair of related lactones belongs to the  $\delta$ -type and which to the  $\gamma$ -type, and since these substances are obtained from sugars by a simple oxidation which does not involve degradation or other profound change, the ring-structure of a sugar derivative can be readily determined.

In many cases the lactones have been submitted to oxidative degradation to the dibasic acids. The characterisation of these degradation products by direct comparison with authentic reference products has furnished confirmation of the structural formulæ which had previously been allocated to the lactones on the basis of the physical studies outlined above. Examples of this kind may be quoted. The crystalline sugar, tetramethyl glucose (I), obtained by methylation methods from  $\alpha$ - or  $\beta$ -methylglucoside, yields a tetramethyl  $\delta$ -gluconolactone (II) which suffers degradation with hot nitric acid. The chief product of this change has been recognised<sup>24</sup> as xylo-trimethoxyglutaric acid (III), which gives a crystalline methylamide identical with that prepared<sup>25</sup> by oxidising the  $\delta$ -lactone (IV) obtained from the trimethyl xylose (V) which is derived from the usual form of methylxyloside.



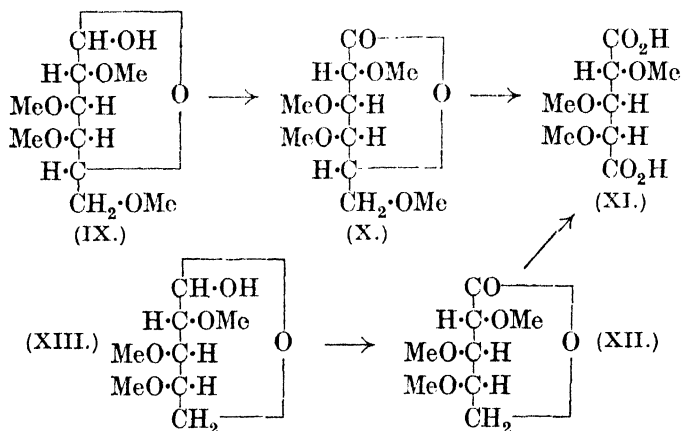
It is conceivable that (III) might arise from the direct oxidation of a tetramethyl sugar of formula (VI), but this is much less likely to be so if the intermediate stage is recognisable as a lactone, since the existence of an  $\epsilon$ -lactone is extremely doubtful. This possibility

<sup>24</sup> W. N. Haworth, E. L. Hirst, and E. J. Miller, *J.*, 1927, 2436; *A.*, 1173.

<sup>25</sup> W. N. Haworth and D. I. Jones, *ibid.*, p. 2349; *A.*, 1059.

is, however, entirely negatived by the experimental observation<sup>26</sup> that the monobasic acid of a substance corresponding to (VI) has been prepared, namely, 2 : 3 : 4 : 5-tetramethyl gluconic acid (VII), and this does not form a lactone, nor does it oxidise to the dibasic acid (III); under the same conditions as those adopted for the degradation of (II) to give (III), it passes into tetramethyl saccharic acid (VIII). It is represented that there can be no other interpretation of these results than that the tetramethyl glucose is correctly formulated by (I) and that  $\alpha$ - and  $\beta$ -methylglucosides possess a six-membered (amylenoxide) ring. That the free  $\alpha$ - and  $\beta$ -glucoses have the same oxide-ring structure seems more than probable.

Referring now to the two aldohexoses galactose and mannose, a confirmation is given that the usual forms of methylgalactoside and also  $\alpha$ -methylmannoside correspond to the same structural classification as the two normal forms of methylglucosides ( $\alpha$ - and  $\beta$ -). Crystalline tetramethyl galactose (IX) yields on oxidation tetramethyl  $\delta$ -galactonolactone (X), the constitution of which is now verified<sup>27</sup> by degradation to the *l*-arabo-trimethoxyglutaric acid (XI), which is identical with that obtained<sup>28</sup> by oxidising *l*-trimethyl  $\delta$ -arabonolactone (XII) and this in turn is obtained from the normal trimethyl arabinose (XIII).



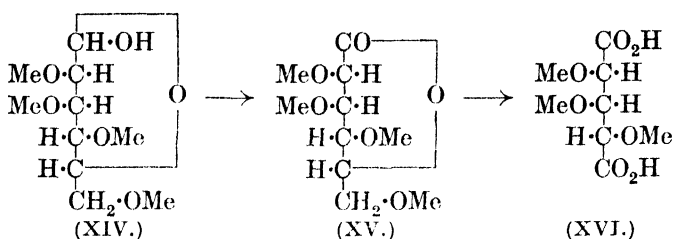
Similarly also with  $\alpha$ -methylmannoside: this yields a tetramethyl mannose (XIV) which passes to a crystalline tetramethyl  $\delta$ -mannonolactone (XV). Degradation of the latter leads to the

<sup>26</sup> W. N. Haworth, J. V. Loach, and C. W. Long, *J.*, 1927, 3146.

<sup>27</sup> W. N. Haworth, E. L. Hirst, and D. I. Jones, *ibid.*, p. 2428; *A.*, 1173.

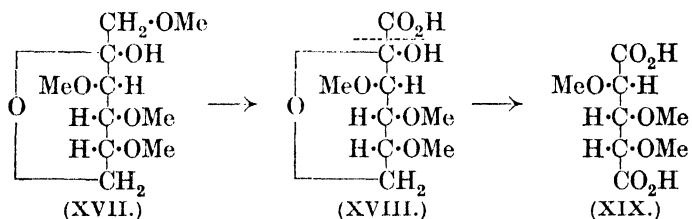
<sup>28</sup> W. N. Haworth and D. I. Jones, *loc. cit.*; J. Pryde and R. W. Humphreys, *J.*, 1927, 559; *A.*, 449.

isolation of *d*-arabo-trimethoxyglutaric acid (XVI),<sup>29</sup> which is the enantiomorph of (XI).



The authors conclude that the usual forms of methylgalactoside and methylmannoside are normal forms in that they are structurally similar to the normal methylglucosides. Galactose and one of the known varieties of mannose seem to possess, therefore, the six-membered ring (amyleno-oxide) structure. This can also be said for the  $\alpha$ - and  $\beta$ -methylarabinosides and methylxylosides, and similarly for ordinary arabinose and xylose.

A like interest attaches to the determination of the structure of  $\beta$ -methylfructoside through its characteristic derivative, crystalline tetramethyl fructose (XVII). The conclusions reported last year<sup>30</sup> have received extended verification in that this sugar is shown definitely to pass on oxidation with nitric acid to the amyleno-oxide lactol-acid (XVIII)<sup>31</sup> and then, by degradation, to *d*-arabo-trimethoxyglutaric acid (XIX), which is identical with (XVI).



It is thus seen that  $\beta$ -methylfructoside possesses the same type of cyclic structure as  $\alpha$ - and  $\beta$ -methylglucosides; and evidently the crystalline fructose, in common with  $\alpha$ - and  $\beta$ -glucose, is suitably represented by the amyleno-oxide formula.

Turning now to the sugar derivatives related to  $\gamma$ -methylglucoside (XX), it is found that the derived tetramethyl  $\gamma$ -glucose (XXI) yields a crystalline tetramethyl  $\gamma$ -gluconolactone (XXII), which passes by oxidative degradation<sup>32</sup> to *d*-dimethoxysuccinic

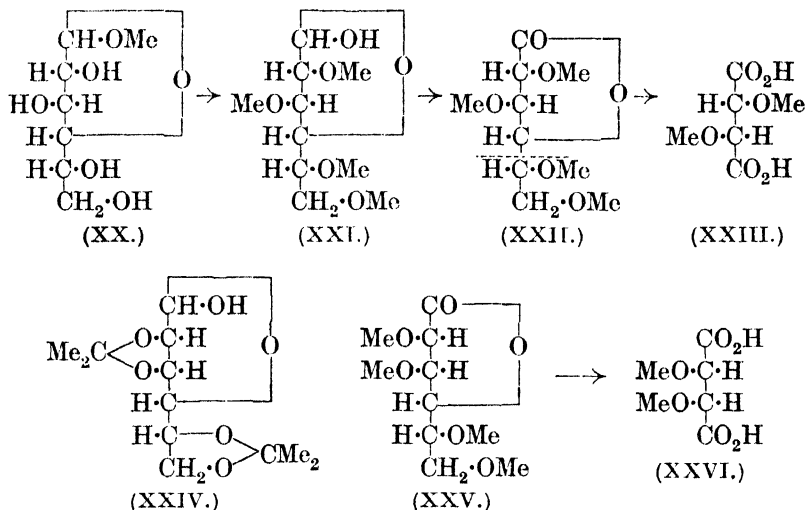
<sup>29</sup> E. H. Goodyear and W. N. Haworth, *J.*, 1927, 3136.

<sup>30</sup> *Ann. Reports*, 1926, 23, 80.

<sup>31</sup> W. N. Haworth, E. L. Hirst, and A. Learner, *J.*, 1927, 1040; *A.*, 649.

<sup>32</sup> W. N. Haworth, E. L. Hirst, and E. J. Miller, *loc. cit.*

acid (XXIII). Direct support is thus given to the butylene-oxide ring formulæ for these derivatives of  $\gamma$ -glucose.



Similarly, tetramethyl  $\gamma$ -mannonolactone (XXV), which has been ascertained to be structurally related to  $\gamma$ -mannose-diacetone (XXIV), gives rise to a degradation product recognisable<sup>33</sup> as *i*-dimethoxysuccinic acid (XXVI). In no case is it observed that a lactone from a  $\gamma$ -sugar derivative yields on oxidation a trimethoxyglutaric acid, and the above evidence permits of no suggestion that an ethylene-oxide or propylene-oxide ring is present in these  $\gamma$ -sugars.

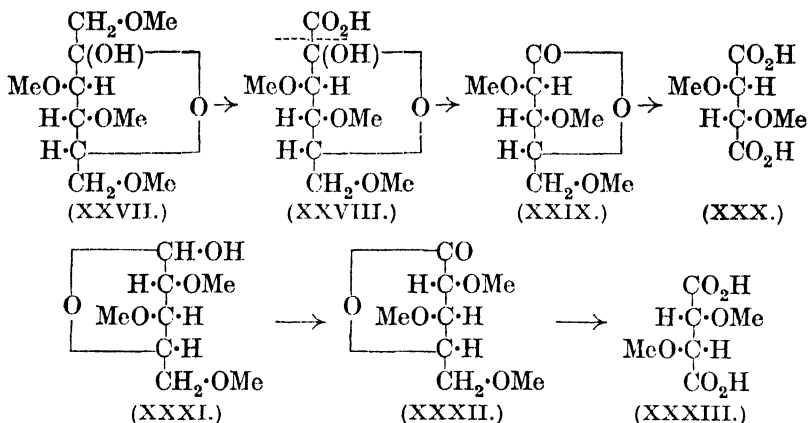
Considerable importance is attached to the observations now recorded that *d*-trimethyl  $\gamma$ -arabonolactone (XXIX) is intimately related to and obtainable from tetramethyl  $\gamma$ -fructose (XXVII). The latter sugar undergoes oxidation with nitric acid to give a butylene-oxidic<sup>34</sup> trimethyl lactol acid (XXVIII) which is degraded by acid permanganate to crystalline *d*-trimethyl  $\gamma$ -arabonolactone. The further oxidation of the latter confirms its previously determined structure, since it has now been degraded<sup>35</sup> to *l*-dimethoxysuccinic acid (XXX), and the crystalline methylamide of the latter is identical with that prepared from *l*-tartaric acid. The enantiomorphic *l*-variety of trimethyl  $\gamma$ -arabonolactone (XXXII), which is derived from the  $\gamma$ -form of trimethyl arabinose (XXXI), gave

<sup>33</sup> E. H. Goodyear and W. N. Haworth, *loc. cit.*

<sup>34</sup> J. Avery, W. N. Haworth, and E. L. Hirst, *J.*, 1927, 2308; *A.*, 1057; W. N. Haworth, E. L. Hirst, and V. S. Nicholson, *ibid.*, p. 1513; *A.*, 859.

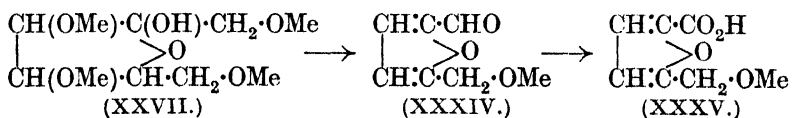
<sup>35</sup> W. N. Haworth, E. L. Hirst, and A. Learner, *ibid.*, p. 2432; *A.*, 1173.

on further oxidation the corresponding *d*-dimethoxysuccinic acid (XXXIII), which was similarly identified.



These experimental results appear to admit only of the interpretation that the  $\gamma$ -lactones derived from methylated aldopentoses had been correctly diagnosed and the butylene-oxide formula applied to tetramethyl  $\gamma$ -fructose in the Report of last year is finally confirmed. It is also clear that the butylene-oxide structure allocated to derivatives of  $\gamma$ -arabinose is established, thus bringing all the known  $\gamma$ -sugars within a comprehensive generalisation.

Collateral evidence of the butylene-oxide character of tetramethyl  $\gamma$ -fructose (XXVII) is furnished by the unexpected observations that this sugar passes with remarkable ease,<sup>36</sup> in contact with either dilute mineral acid or with acetic anhydride and sodium acetate, into  $\omega$ -methoxymethylfurfural (XXXIV), which was identified through its oxime and semicarbazone as well as through the corresponding acid (XXXV). The latter was compared with authentic crystalline  $\omega$ -methoxymethylfurancarboxylic acid prepared from ordinary fructose and also from glucosamine by the Fischer transformation of chitonic acid to  $\omega$ -hydroxymethylfurfural.



A mechanism for these transformations is advanced in explanation of the probable consecutive changes leading to the furan compounds. In this connexion it is also of interest to notice that  $\omega$ -hydroxymethylfurfural is formed from pine lignin by steam.<sup>37</sup>

<sup>36</sup> W. N. Haworth, E. L. Hirst, and V. S. Nicholson, *loc. cit.*

<sup>37</sup> W. Fuchs, *Ber.*, 1927, **60**, 1131; *A.*, 650.



Two crystalline derivatives of  $\gamma$ -glucose have now been isolated as the  $\alpha$ - and  $\beta$ -forms of pentabenzoyl  $\gamma$ -glucose.<sup>38</sup> Their specific rotations ( $[\alpha]_D + 58.6^\circ$  and  $-52.6^\circ$ ) differ widely from those of the corresponding normal glucose derivatives ( $+ 107.6^\circ$ ;  $+ 23.7^\circ$ ). The latter values correspond fairly closely to those of  $\alpha$ - and  $\beta$ -glucose ( $+110^\circ$ ;  $+17.5^\circ$ ) and from these comparisons it may be surmised that, were it possible to isolate the two  $\gamma$ -forms of the free sugar, the  $\alpha$ -form would have a much lower positive rotation than the normal or usual form of  $\alpha$ -glucose, whereas the  $\beta$ -form of  $\gamma$ -glucose would be strongly laevorotatory. Again, the above rotations of  $\alpha$ - and  $\beta$ -glucose are comparable in their range with the values of the normal  $\alpha$ - and  $\beta$ -methylglucosides, and it would appear that the two stereoisomeric forms of  $\gamma$ -methylglucoside may be expected to possess specific rotations similar in range to the above pentabenzoyl derivatives of  $\gamma$ -glucose, the  $\beta$ -form of  $\gamma$ -methylglucoside having a much higher laevorotation than the normal  $\beta$ -methylglucoside.

Tetramethyl  $\gamma$ -glucose is given an equilibrium rotation of  $[\alpha]_D -11^\circ$  and it is reported<sup>39</sup> that the m. p. of one form is slightly above  $0^\circ$ . It has again been shown that this sugar is formed in a series of stages from glucose-diacetone, to which is therefore attributed the butylene-oxide structure of a  $\gamma$ -sugar. A view expressed in last year's Report, that in the formation of glucose-diacetone from crystalline glucose the amylen-oxide ring of the latter undergoes displacement, is supported by the authors of the same paper.

The use of the expression "normal sugar" was admitted to the terminology of the sugar group for the reason that it served to distinguish those sugar derivatives related to the "normal"  $\alpha$ - and  $\beta$ -methylglucosides from the so-called " $\gamma$ -sugars," which were related to the less stable  $\gamma$ -methylglucoside isolated by Fischer in 1914. Derivatives of sugars other than glucose have also been referred to the same two normal structural types, represented by  $\alpha$ - and  $\beta$ -methylglucosides on the one hand and by  $\gamma$ -methylglucoside on the other.

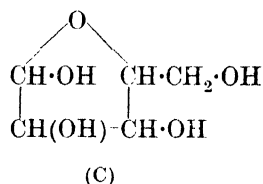
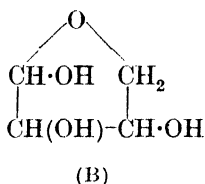
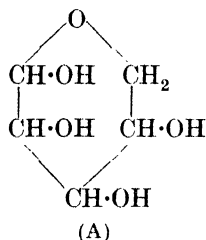
The  $\alpha$ - and  $\beta$ -methylarabinosides are normal in the sense that both are structurally related to  $\alpha$ - and  $\beta$ -methylglucosides, and in the same category are also  $\beta$ -methylxyloside,  $\beta$ -methylgalactoside,  $\alpha$ -methylmannoside,  $\beta$ -methylfructoside, and  $\alpha$ -methylrhamnoside. Thus the common forms of methylhexosides and pentosides are "normal" and possess the amylen-oxide structure. Future work will doubtless reveal crystalline methylhexosides and pentosides

<sup>38</sup> H. H. Schlubach and W. Huntenberg, *Ber.*, 1927, **60**, 1487; *A.*, 858.

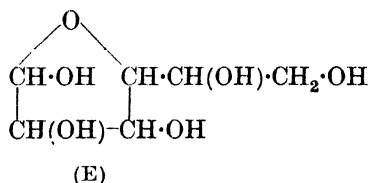
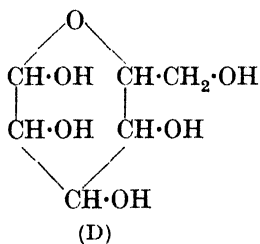
<sup>39</sup> F. Micheel and K. Hess, *Annalen*, 1926, **450**, 21; *A.*, 1927, 43.

which conform to the butylene-oxide type of  $\gamma$ -methylglucoside, which is at present recognised only as a liquid mixture of two stereochemical forms.

Knowledge of the structure of sugars has reached a stage at which, it is suggested,<sup>40</sup> confusing terms such as normal,  $\gamma$ -, h-, amylen-oxide, butylene-oxide, 1 : 5-oxide, 1 : 4-oxide might conveniently be replaced by a reformed nomenclature having a definite relation to the structure and configuration of the sugars. It is seen that the parent form of "normal" or amylen-oxide sugars is represented by pyran, and of the  $\gamma$ - or butylene-oxide sugars by furan,

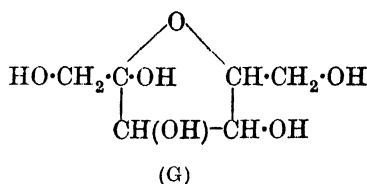
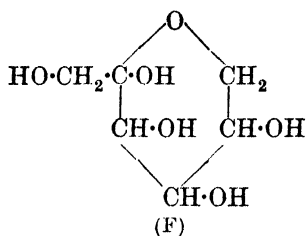


and thus the reduced and hydroxylated parent forms represent the simplest sugars. For example, (A) is an expression of the simplest normal pentose, and (B) is that of the simplest tetrose—a  $\gamma$ -sugar. (A) and (B) may conveniently be named pyranose and furanose. The simplest  $\gamma$ -pentose would be (C), wherein a side chain is attached to (B). The configuration of each sugar may be represented by the prefix xylo-, arabo-, etc., so that the spatial distribution of the hydroxyl groups, as well as the ring structure, would be clearly defined by a terminology: xylo-pyranose, arabo-pyranose, etc., and xylo-furanose, arabo-furanose, etc.



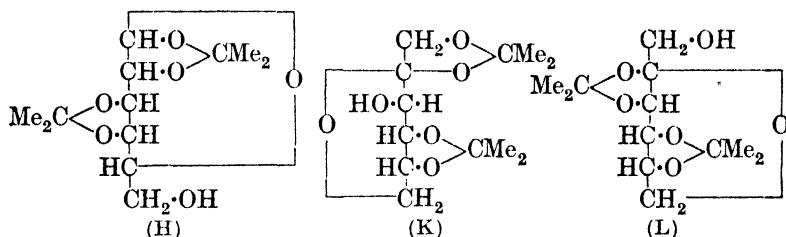
Similarly the two types of hexoses (D) and (E) may be termed glucopyranose and gluco-furanose, and the variation of the prefix to manno-, galacto-, etc., would define the structure and configuration of the remaining aldohexoses.

<sup>40</sup> E. H. Goodyear and W. N. Haworth. *loc. cit.*



The expressions fructo-pyranose (F) and fructo-furanose (G) correctly define the two constitutional forms of fructose.

It must, however, be kept in view that both aldoses and ketoses may, and probably do, react also as the open-chain aldehyde and keto-forms, and that this transitional phase is present in sugar solutions which are undergoing or have undergone mutarotation. In the condition of equilibrium it is by no means impossible to contemplate that the pyranose, furanose, and open-chain types of sugars may all be present; but in the case of glucose, which has been most widely studied, there seems little doubt that the pyranose type preponderates even in aqueous solution. This problem is engaging the attention of physical chemists, and a clear statement of the present position of this line of inquiry has been contributed. The account of this given by T. M. Lowry<sup>41</sup> serves also to summarise the most recent results obtained in the study of the mutarotation of glucose and its derivatives in various solutions, and reference should be made to this interesting paper.



The synthesis of the natural glucoside coniferin is reported.<sup>42</sup> This has been effected by condensing acetobromoglucose with the potassium derivative of 4-hydroxy-3-methoxycinnamaldehyde, and hydrolysis of the acetyl residues in the product.

The synthesis of indican<sup>43</sup> has been accomplished by the interaction of methyl 3-hydroxyindole-2-carboxylate with acetobromoglucose in acetone solution containing potassium hydroxide.

<sup>41</sup> *Z. physikal. Chem.*, 1927, **130**, 125.

<sup>42</sup> H. Pauly and K. Feuerstein, *Ber.*, 1927, **60**, 1031; *A.*, 649.

<sup>43</sup> A. Robertson, *J.*, 1927, 1937.

Hydrolysis of the acetyl groups yielded 3-hydroxyindole-2-carboxylic acid- $\beta$ -glucoside. Heating with sodium acetate and acetic anhydride led to the elimination of the carboxyl group and also to the formation of an acetylated product, which was identical with penta-acetylindican. The latter was deacetylated with methyl-alcoholic ammonia and gave indican, identical with the natural glucoside.

Two glucosides of alizarin have also been synthesised,<sup>44</sup> but neither of these is found to be identical with ruberythric acid.

Some progress has been made in redetermining the constitution of the acetone-sugars, since the earlier formulæ are of doubtful validity. It is demonstrated that galactose-diacetone<sup>45</sup> is to be represented by (H) (since it is convertible into fucose-diacetone); and  $\alpha$ - and  $\beta$ -fructose-diacetones<sup>46</sup> by (K) and (L).

*Disaccharides.*—The synthesis of disaccharides by simple and direct union of hexoses constitutes a new and facile method.<sup>47</sup> It is reported that maltose is obtained by heating equal weights of  $\alpha$ - and  $\beta$ -glucose at 160° in a vacuum. Similarly, lactose is said to be formed by heating  $\beta$ -glucose and  $\beta$ -galactose for 30 minutes at 150°/15 mm. in presence of zinc chloride, and melibiose, according to the same authors, is formed with almost equal facility.

Galactose-diacetone condenses with acetobromoglucose with the formation of a substituted disaccharide.<sup>48</sup> The free biose was isolated as a dextrorotatory 6-glucosido-galactose. A synthesis of the naturally occurring primeverose has been accomplished by combining<sup>49</sup> 1 : 2 : 3 : 4-tetra-acetyl glucose and acetobromoxylose and hydrolysing the hepta-acetate to the disaccharide. The constitution of this sugar is therefore found to be (I) and it is probably formed in nature from gentiobiose.

The structural formula (II) deduced by earlier authors for maltose<sup>50</sup> has been investigated by the progressive degradation of the biose through its oxime to a glucose-arabinose, which forms an osazone, and finally to a glucose-erythrose (III), which is found to be incapable of forming an osazone.<sup>51</sup> It is argued that the biose linking in the latter must engage the second hydroxyl group in the erythrose chain, which is the equivalent of the fourth hydroxyl group in the

<sup>44</sup> E. Glaser and O. Kahler, *Ber.*, 1927, **60**, 1349; **A.**, 752.

<sup>45</sup> K. Freudenberg and K. Raschig, *ibid.*, p. 1633; **A.**, 858.

<sup>46</sup> H. Ohle, *ibid.*, p. 1168; **A.**, 649.

<sup>47</sup> A. Pictet and H. Vogel, *Compt. rend.*, 1927, **184**, 1512; **185**, 332; **A.**, 752, 960; *Helv. Chim. Acta*, 1927, **10**, 280; **A.**, 450.

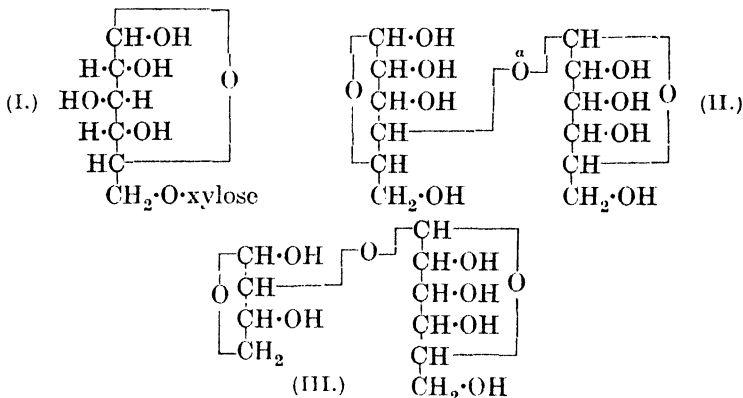
<sup>48</sup> K. Freudenberg, A. Noë, and E. Knopf, *Ber.*, 1927, **60**, 238; **A.**, 230.

<sup>49</sup> B. Helferich and H. Rauch, *Annalen*, 1927, **455**, 168; **A.**, 859.

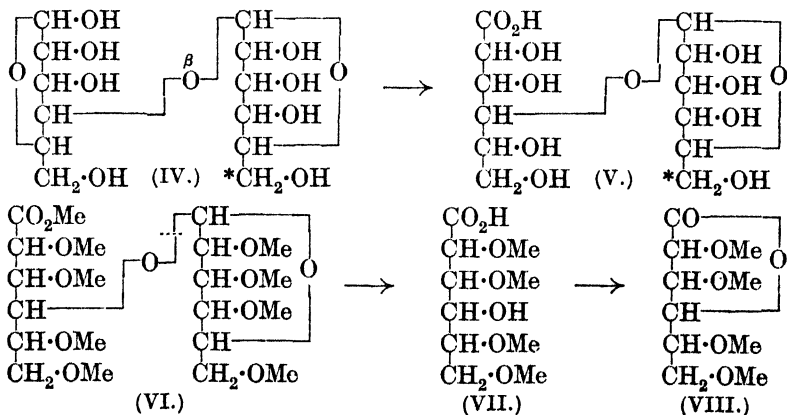
<sup>50</sup> W. N. Haworth and S. Peat, *J.*, 1926, 3094; **A.**, 1927, 135.

<sup>51</sup> G. Zemplén, *Ber.*, 1927, **60**, 1555; **A.**, 859.

reducing glucose residue in the original maltose. The formula (II) receives support from these conclusions, and also from the observations of other authors who have studied the rate of lactone formation from maltobionic acid.<sup>52</sup> The results indicate that the biose linking is at position 4 in the gluconic acid residue and that a six-ring lactone is formed by union of the acid group with the hydroxyl at position 5.



Cellobiose (IV) is shown by the following observations to be built up on the same structural plan as maltose. Oxidation of the biose to cellobionic acid (V), followed by esterification and methylation, yielded methyl octamethylcellobionate (VI) and by hydrolytic cleavage there were isolated the crystalline 2 : 3 : 4 : 6-tetramethyl glucose, and also 2 : 3 : 5 : 6-tetramethyl gluconic acid (VII), which gave on heating the corresponding crystalline 2 : 3 : 5 : 6-tetramethyl  $\gamma$ -gluconolactone (VIII). This was identical with a specimen previously isolated from (a) methyl octamethylmaltobionate and

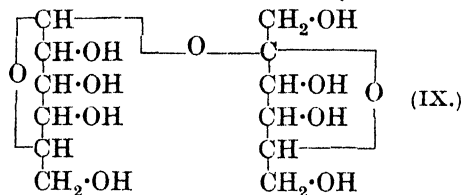


<sup>52</sup> P. A. Levene and H. Sobotka, *J. Biol. Chem.*, 1927, **71**, 471.

also from (b) 2 : 3 : 5 : 6-tetramethyl  $\gamma$ -glucose, the structure of which had already been determined by oxidation methods. The constitutional formula (IV) which had previously been determined by other methods and by the same authors<sup>53</sup> is thus confirmed.

An analogous investigation was undertaken to determine the structure of lactose. Lactobionic acid gave on methylation methyl octamethyl-lactobionate, which on hydrolysis yielded crystalline 2 : 3 : 4 : 6-tetramethyl galactose and 2 : 3 : 5 : 6-tetramethyl gluconic acid (VII). The latter acid was transformed by heat into the same crystalline lactone (VIII) as that which was isolated also from (a) methyl octamethylmaltobionate, (b) methyl octamethyl-cellobionate, (c) 2 : 3 : 5 : 6-tetramethyl  $\gamma$ -glucose. It follows that lactobionic acid<sup>54</sup> has the same structural formula as cellobionic acid, modified, however, by having a galactose instead of a glucose residue at the position marked \* in the formula (V). The constitution allocated to lactose by previous authors is again confirmed by these data. The revision of the formula of glucose has served admirably the general plan for the formulation of the disaccharides; and the determinations of constitution of lactose, cellobiose, gentiobiose, and melibiose during the pre-revision period fall naturally into the newer system of expression in which the constituent hexoses are shown as amylenc-oxides or pyranoses. Maltose also conforms to this general plan.

A disaccharide formula which has been affected by the revision of the older oxide-ring applied to the simple hexoses is that of sucrose. It is now shown that normal fructose is an amylene oxide or pyranose, and that the older butylenc-oxidic formula assigned to this ketose must now be allocated to the  $\gamma$ -fructose, which is the component occurring in sucrose. It is thus established that the normal sugars which have been so far investigated are based on a common pyranose structure, whether aldoses or ketoses, and  $\gamma$ -fructose takes its place



alongside the  $\gamma$ -aldoses as a butylene-oxide (or furanose) form. The proofs leading to this conclusion are given in the section under monosaccharides,<sup>55</sup> but since the tetramethyl  $\gamma$ -fructose isolated from methylated sucrose has been utilised as the material on which

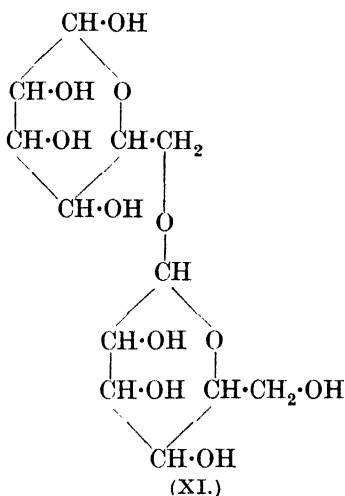
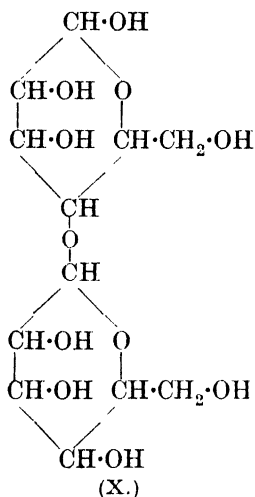
<sup>53</sup> W. N. Haworth, C. W. Long, and J. H. G. Plant, *J.*, 1927, 2809.

<sup>54</sup> W. N. Haworth and C. W. Long, *ibid.*, p. 544; *A.*, 450.

<sup>55</sup> See pp. 71, 74.

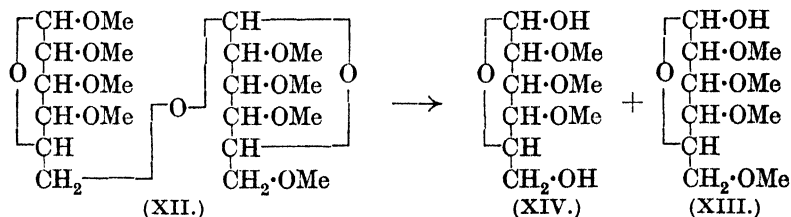
the investigation is based, the structural formula of sucrose (IX) was naturally the main issue in these determinations, and this formula, advanced last year, has received substantial confirmation.

Whereas maltose, cellobiose and lactose are similarly constituted in that (their essential stereochemical differences being neglected) they are all structurally represented by the formula (X),



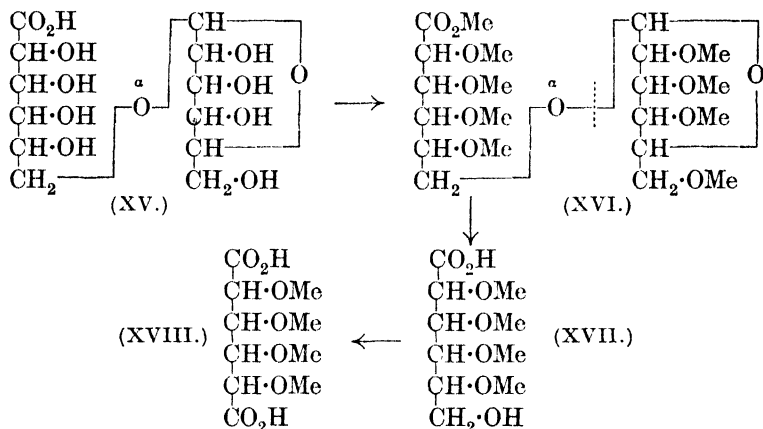
the important bioses gentiobiose and melibiose conform to the structural type (XI) wherein the non-reducing hexose component is attached to the reducing component through a hydroxyl linked to the side chain of the latter, and not to a hydroxyl attached to the ring as in (X).

These formulæ for gentiobiose and melibiose were advanced some years ago. The constitution of gentiobiose was verified last year by synthesis, and this structure for melibiose is strongly supported by two further papers.<sup>56</sup> Methylated melibiose (XII) gave on hydrolytic cleavage the crystalline 2 : 3 : 4 : 6-tetramethyl galactose (XIII) and also 2 : 3 : 4-trimethyl glucose (XIV), recognised as its crystalline glucoside.

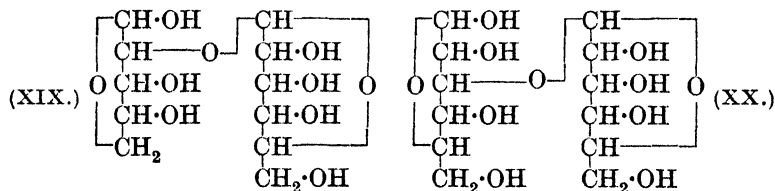


<sup>56</sup> W. Charlton, W. N. Haworth, and W. J. Hickinbottom, *J.*, 1927, 1527; *A.*, 859; W. N. Haworth, J. V. Loach, and C. W. Long, *ibid.*, p. 3146.

The union of these two hydrolytic fragments could only have existed through the exposed hydroxyl in the terminal position in (XIV), from which it follows that methylated melibiose has the structure (XII) and the free disaccharide the corresponding formula, indicated also in another way in (XI). Again, melibiose gave on oxidation with bromine melibionic acid (XV); and this structural formula alone could be applied to it, since the fully methylated melibionic ester (XVI) gave rise on hydrolytic cleavage to crystalline tetramethyl galactose (XIII) and to tetramethyl gluconic acid (XVII) which, on further oxidation, was transformed into the tetramethyl saccharic acid (XVIII).



This structural formula for melibiose has been attacked by G. Zemplén,<sup>57</sup> who, by degrading the sugar through its oxime, failed to isolate either the galacto-arabinose or its crystalline phenylosazone. The author attributes this failure to the presence of the biose linking in the position shown below in the galacto-arabinose (XIX), since this would prevent osazone formation; and the formula suggested by the same author for melibiose is (XX).

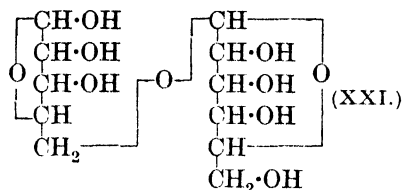


An alternative reason for the difficulty experienced by the author in isolating the expected products may well be that on the basis of the melibiose formula (XI) which he attacks, the galacto-arabinose

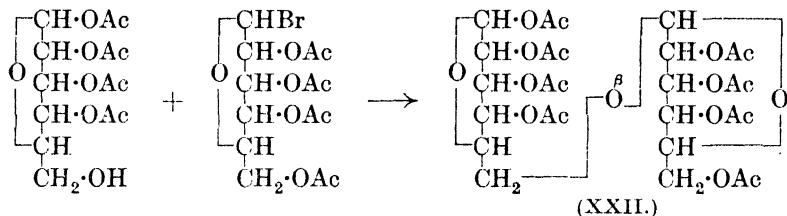
<sup>57</sup> Ber., 1927, 60, 923; A., 545.



obtained by degradation would be a butylene-oxide or  $\gamma$ -sugar (XXI), and hitherto no crystalline osazone of this labile type has been isolated.



The synthesis of a new disaccharide has been effected as follows : 1 : 2 : 3 : 4-tetra-acetyl glucose was condensed with acetobromogalactose in presence of silver oxide. The resulting octa-acetate of the glucose- $\beta$ -galactoside (XXII) was not identical with melibiose octa-acetate, nor was the liberated disaccharide the same as melibiose.



These authors<sup>58</sup> rightly conclude that either the configuration of melibiose as a  $\beta$ -galactoside is incorrect or the structure previously ascribed to this biose (XI) is untenable. The configuration given to melibiose in the literature is based on the observation<sup>59</sup> that this sugar is hydrolysed slowly by emulsin. Other authors<sup>60</sup> are unable to accept the interpretation which has been given to this evidence based on enzyme cleavage, and support the argument that melibiose, having the recognised structure (XI), cannot be a glucose- $\beta$ -galactoside, since on this assumption its high rotation is in disagreement with Hudson's rule and with other data. On the view that melibiose is a glucose- $\alpha$ -galactoside, corresponding with maltose as glucose- $\alpha$ -glucoside, the newly observed facts can be reconciled.

The constitutional formula ascribed to turanose and reported last year has received experimental support from another worker, who outlines a much more convincing proof of the character of the trimethyl  $\gamma$ -fructose component isolated from methylated

<sup>58</sup> B. Helferich and H. Rauch, *Ber.*, 1926, **59**, 2655; *A.*, 1927, 44.

<sup>59</sup> E. Fischer and E. F. Armstrong, *Ber.*, 1902, **35**, 3144.

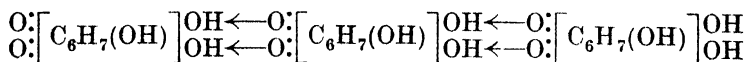
<sup>60</sup> W. Charlton, W. N. Haworth, and W. J. Hickinbottom, *loc. cit.*; W. N. Haworth, J. V. Loach, and C. W. Long, *loc. cit.*

melezitose. The constitutional formula for the trisaccharide melezitose appears, therefore, to be established.<sup>61</sup> There are, however, difficulties in interpreting the behaviour of enzymes towards this sugar, in that a preparation from *Aspergillus niger*, which acts slowly on sucrose, attacks melezitose rapidly, and one author suggests that the sucrose residue does not occur in melezitose.

A new trisaccharide has been synthesised by condensing 1 : 2 : 3 : 4-tetra-acetyl glucose with acetobromocellobiose in presence of silver oxide. The trisaccharide<sup>62</sup> was isolated as a crystalline substance and gave a crystalline osazone. It does not appear to be identical with a natural product.

*Polysaccharides*.—There seems little prospect of the cessation of interest in the allocation of new structural formulæ to the chief members of the group of polysaccharides. The volume of experimental work contributed on this subject grows apace, and if a generalisation on them be expected of the Reporter, it must be said that the more recent results have proved the futility of all attempts to express the formulation of cellulose or starch until our knowledge of many underlying problems has outgrown its present limitations. Determinations of molecular weights of derivatives of the polysaccharides lead in many cases to precarious reasoning, particularly when, as is too often the case, the products examined are amorphous mixtures. The contest is proceeding between rival theories concerning the factors which are operative in the complex aggregations in polysaccharides.

One view of the constitution of polysaccharides postulates the existence of a comparatively simple structural unit<sup>63</sup> which retains its definite entity while existing in a highly associated form. Under selected conditions there may be a lesser degree of association operative in certain solvents, which means that the solute undergoes dispersion. Presumably the linkages responsible for this association are not those of ordinary valency. The only alternative seems to be to regard these as being due to the operation of co-ordinate co-valencies on the model of N. V. Sidgwick's suggestions.<sup>64</sup> This renders the formula originally suggested by K. Hess a very attractive one,



<sup>61</sup> (Miss) G. C. Leitch, *J.*, 1927, 588; *A.*, 450; M. Bridel and C. Aagaard, *Compt. rend.*, 1927, 185, 147; *A.*, 859.

<sup>62</sup> B. Helferich and W. Schäfer, *Annalen*, 1926, 450, 229; *A.*, 1927, 135.

<sup>63</sup> M. Bergmann, *Annalen*, 1927, 452, 121; *A.*, 341. Compare *Ann. Reports*, 1924, 21, 91.

<sup>64</sup> Presidential Address to Section B, *Brit. Assoc. Reports*, 1927.

It is difficult, however, to conceive of the persistence of these co-ordinate links when the hydroxyl groups of cellulose have been replaced by methoxyl or acetoxyl groups, and if for no other reason, it would appear that this consideration renders the formula of Hess difficult of acceptance.

On another plan, the simple structural unit is held to polymerise to a higher unit or to higher units of varying complexity by structural change.<sup>65</sup> The breakdown of these complexes is then a step-wise process ending with the simplest possible form, which can again revert to the more complex state. In this connexion, the illuminating example of *l*-trimethyl  $\delta$ -arabonolactone may be cited. This crystalline substance polymerises with extreme readiness to a polymeric crystalline form, which has ten times the molecular weight of the original lactone and reverts to the simple lactone on heating. There seems to be on the whole little difference in principle between this second view of a polymerised unit and the traditional view which adopts the conception of hexose rings linked by connecting oxygen atoms in a chain of indefinite length by the operation of ordinary valency. It does not seem to be an essential consideration that the unit which undergoes polymerisation should retain, on this second plan, its structure in the polymerised aggregate, nor does it necessarily follow that the process of depolymerisation to the simplest unit would always be attainable. A modification of the older, traditional formula has been advanced and has been based on a study of the X-ray spectrograph of cellulose in ramie fibre. The linkings between the constituent hexose rings, according to this formula, engage in alternative pairs the 1 : 1-hydroxyl groups and the 4 : 4-hydroxyl groups.<sup>66</sup> It is also suggested that lateral contact with hydroxyl groups of adjoining chains establishes a further type of union by the functioning of subsidiary valency forces (co-ordinate valencies) which are more readily dissipated or overcome.

Were it possible to select from these and other current theories a simple working hypothesis which reconciled a large number of experimental facts, there would remain, at the present juncture, the further difficulty of deciding which is the fundamental structural unit of any one polysaccharide. The idea is now on trial that a form of glucose anhydride constitutes such a unit of cellulose,<sup>67</sup>

<sup>65</sup> H. Staudinger, H. Johner, R. Signer, G. Miß, and J. Hengstenberg, *Z. physikal. Chem.*, 1927, **126**, 425; **A.**, 647.

<sup>66</sup> O. L. Sponsler and W. H. Dore, Colloid Symposium Monograph (California), 1926, No. 4, p. 174. Compare *Nature*, 1927, **120**, 767.

<sup>67</sup> K. Hess and his collaborators, *Annalen*, 1926, **450**, 29, 40, 65; 1927, **455**, 81, 205; 1927, **456**, 38, 55; **A.**, 1927, 44, 753, 861.

lichenin,<sup>68</sup> glycogen,<sup>69</sup> and the amylose of starch<sup>70</sup>; and that inulin is similarly an associated fructose anhydride.<sup>71</sup> This conception rests largely on the determinations of molecular weights of the triacetates of polysaccharides in special solvents, *e.g.*, air-free acetic acid. In ordinary acetic acid inulin triacetate gives exactly twice this value, as indeed does inulin dissolved in ammonia, and other workers have in consequence identified the structural unit of fructose with difructose anhydride,<sup>72</sup> a view which is tenaciously held.

Another formula applied to the cellulose unit, namely, that of an anhydrotriglucose, meets with direct opposition.<sup>73</sup> It will also be remembered that the constitution of an anhydrohexaglucose has been recently applied to one of the constituents of starch.<sup>74</sup>

Again, if the simplest of these conceptions were to be accepted, allocation of a structural formula to the polysaccharide would have to take account of and define the centres of those forces which promote the aggregation of such a simple unit.

K. Hess and his collaborators<sup>75</sup> have prepared a simple methylated glucose anhydride (I) from the actual 2 : 3 : 6-trimethyl glucose to which methylated cellulose, starch and glycogen give rise on complete hydrolysis. This product has none of the properties of a methylated polysaccharide, and the authors are led to conclude that the cryoscopic behaviour of trimethyl cellulose in glacial acetic acid must be ignored or that the structure of the cellulose cannot be based on the isolation of 2 : 3 : 6-trimethyl glucose.

In the face of many highly conflicting opinions which are ill-supported by ascertained facts, it is clearly inopportune to pronounce upon any of the contending principles which are now on their trial. It seems probable that the succeeding year will witness the accession of a more intimate and fundamental knowledge based

<sup>68</sup> H. Pringsheim and O. Rontala, *Annalen*, 1926, **450**, 255; *A.*, 1927, 136; M. Bergmann and E. Knehe, *ibid.*, 1927, **452**, 151; *A.*, 341; K. Hess and H. Friese, *ibid.*, 1927, **455**, 180; *A.*, 860.

<sup>69</sup> K. Hess and R. Stahn, *ibid.*, p. 115; *A.*, 753.

<sup>70</sup> M. Bergmann and E. Knehe, *ibid.*, 1927, **452**, 141; *A.*, 342; A. Pictet and R. Salzmänn, *Helv. Chim. Acta*, 1927, **10**, 276; *A.*, 450. Compare H. Pringsheim and P. Meyersohn, *Ber.*, 1927, **60**, 1709; *A.*, 860.

<sup>71</sup> K. Hess and R. Stahn, *Annalen*, 1927, **455**, 104; *A.*, 753.

<sup>72</sup> M. Bergmann and E. Knehe, *ibid.*, 1926, **449**, 302; *A.*, 1926, 1230. Compare L. Schmidt and G. Bilowitzki, *Monatsh.*, 1927, **47**, 768; **48**, 163; *A.*, 342, 861.

<sup>73</sup> K. Hess and F. Micheel, *Annalen*, 1927, **456**, 69; *A.*, 1058.

<sup>74</sup> See *Ann. Reports*, 1923, **20**, 83. Compare A. R. Ling, *J. Soc. Chem. Ind.*, 1927, **46**, 279; *A.*, 860.

<sup>75</sup> F. Micheel and K. Hess, *Ber.*, 1927, **60**, 1898; *A.*, 1056.

on new experimental methods of approach to the problem. Meantime it is considered more appropriate to review the general trend of thought than to attempt to appraise the very numerous and disconnected publications which bear on the subject.

### *Acids.*

The use of a mixture of iodine, red phosphorus, and phosphorus pentachloride as a catalytic agent for the chlorination of acetic acid enables the preparation of pure monochloroacetic acid to be carried out rapidly and conveniently without the aid of light.<sup>76</sup> Examples of the reducing action of acetic anhydride have been recorded, hydrated cupric sulphate and chloride being reduced to the corresponding anhydrous cuprous salts on continued boiling with the reagent. Similar reactions with mercuric salts lead to the formation of complex mercurous compounds, that of the chloride being stable whereas the sulphate suffers reduction to metallic mercury.<sup>77</sup>

A study of the effect of *gem*-dialkyl groups on the formation and stability of the anhydrides of dicarboxylic acids has shown that adipic and  $\beta$ -methyladipic acids form unimolecular anhydrides which are readily hydrolysed by atmospheric moisture, and can be formed by the action of acetic anhydride on the acid. A progressive increase in stability is found with the  $\beta\beta\beta'\beta'$ - and  $\alpha\alpha\alpha'\alpha'$ -tetramethyladipic acids, the former being stable to boiling water and to sodium carbonate solution.<sup>78</sup>

Glycols and  $\alpha$ -hydroxy-acids react readily with chloral hydrate on warming in the presence of sulphuric acid to give chloralides. From lactic acid a solid product, m. p.  $45^\circ$ , is obtained without evidence of the formation of *cis*- and *trans*-isomerides. From *d*-tartaric acid a mixture of isomerides is formed from which two crystalline dichloralides, m. p.  $116$ — $118^\circ$ ,  $[\alpha]_D^{25}$ — $33.1^\circ$ , and m. p.  $159$ — $161^\circ$ ,  $[\alpha]_D^{25}$ — $53.9^\circ$  in chloroform, have been isolated. With salicylic acid and amygdalic acid condensation takes place so readily that the presence of sulphuric acid is unnecessary.<sup>79</sup>

The action of hydrogen under pressure, in the presence of aluminium oxide and nickel oxide, on heated solutions of the sodium salts of lactic, citric, pyruvic, and of various substituted hydroxy-succinic acids results in the reduction of the hydroxyl group with ultimate production of methylsuccinic acid along with various products resulting from scission of the molecule. The primary

<sup>76</sup> H. Brückner, *Z. angew. Chem.*, 1927, **40**, 973; *A.*, 959.

<sup>77</sup> J. B. Menke, *Rec. trav. chim.*, 1926, **45**, 908; *A.*, 131.

<sup>78</sup> E. H. Farmer and J. Kracovski, *J.*, 1927, 880; *A.*, 447.

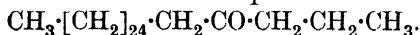
<sup>79</sup> J. Böeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 55; *A.*, 646. See also F. H. Yorston, *Rec. trav. chim.*, 1927, **46**, 711; *A.*, 1171.

product of the change in such cases is thought to be lactic acid, which then undergoes the following transformations :

$2\text{HO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na} \longrightarrow \text{CO}_2\text{Na}\cdot\text{CMe}(\text{OH})\cdot\text{CHMe}\cdot\text{CO}_2\text{Na} \longrightarrow \text{CO}_2\text{Na}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Na} \longrightarrow \text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ . In each case methylsuccinic acid was isolated, but the intermediate  $\alpha$ -hydroxy- $\alpha\beta$ -dimethylsuccinic acid could not be detected. Sodium malate, tartrate and glycollate give some succinic acid under the above conditions, but the main products are methane, formic and acetic acids and their sodium salts, and carbon dioxide.<sup>80</sup>

The long-chain fatty acids continue to attract attention and a considerable advance in detailed knowledge of these substances has to be recorded in this section. A series of higher fatty acids having a methyl group in the  $\alpha$ -position has been synthesised and studied, particularly from the point of view of physical properties. It is concluded that the length of the unbroken chain rather than the total number of carbon atoms present governs the alternating effect noticeable in the m. p.'s of this series of acids, and that the naturally occurring acids which have lower m. p.'s than the corresponding normal isomerides are not methyl derivatives, but contain branch chains, if the isomerism is due to this cause, at a point remote from the carboxyl group.<sup>81</sup>

The oxidation of synthetic *n*-triacontane has been shown to proceed very similarly to that of natural paraffin wax. The highest acid identified was cerotic acid with a carbon chain of 26 atoms. The mechanism of the reaction appears to involve the formation of a secondary alcohol as the primary product, which then passes into a ketone containing 30 carbon atoms. X-Ray analysis indicates that the oxygen is situated on the fourth carbon atom and evidence is available to show that the ketone possesses the formula



It seems probable that simultaneously with the formation of the secondary alcohol further oxidation may take place, producing polyhydroxy-derivatives which then yield ketones and acids.<sup>82</sup> Aleuritic acid from shellac has been further examined by oxidative methods, 3% potassium hydroxide solution giving azelaic acid and  $\zeta$ -hydroxyheptoic acid. Under other conditions, azelaic and pimelic acids and non-crystalline aldehydic compounds are obtained, and the evidence as a whole is interpreted as showing aleuritic acid to be  $\theta$ -trihydroxypalmitic acid.<sup>83</sup>

<sup>80</sup> V. Ipatiev and G. Rasuwajew, *Ber.*, 1927, **60**, 1971, 1973; G. Rasuwajew, *ibid.*, p. 1976; **A.**, 1053, 1054.

<sup>81</sup> G. T. Morgan and E. Holmes, *J. Soc. Chem. Ind.*, 1927, **46**, 152; **A.**, 539.

<sup>82</sup> F. Francis and H. F. Gauntlett, *J.*, 1926, 2377; **A.**, 1926, 1119; F. Francis and N. E. Wood, *J.*, 1927, 1897; **A.**, 956.

<sup>83</sup> W. Nagel, *Ber.*, 1927, **60**, 605; **A.**, 447.

A general method for the preparation of  $\alpha\beta$ -unsaturated acids is described according to which an aldehyde, dissolved in anhydrous ether, is allowed to react with malonic acid in the presence of dry pyridine at a temperature regulated to suit the reactivity of the aldehyde. In this way pentenoic acid may readily be obtained.<sup>84</sup>

Attention has again been directed to the problem of obtaining pure oleic acid, and two methods have been described during the year for freeing oleic acid from higher saturated and unsaturated acids. One<sup>85</sup> of these employs recrystallised lithium oleate, which is decomposed with hydrochloric acid, and the other<sup>86</sup> makes use of the complex compound of mercury and oleic acid which is prepared from the crude acid, mercuric acetate, acetic acid and methyl alcohol. By the latter method a product is obtained which contains less than 0.5% of saturated acids. The purified acid is dimorphous and may be obtained either in the form of transparent colourless needles, m. p. 13°, or as a more stable opaque modification, m. p. 16°.

The action of perbenzoic acid on oleic acid gives a solid oxide, m. p. 58°, which may be hydrolysed with dilute acids to a solid dihydroxystearic acid, m. p. 94°, whereas the oxide corresponding to elaidic acid gives a dihydroxystearic acid, m. p. 137°. The authors<sup>87</sup> accept the older view of the relationship of oleic to elaidic acid whereby the dihydroxystearic acid of high melting point is said to correspond to oleic acid, and they are thus forced to adopt the idea that isomerisation occurs during hydrolysis of the oxide. This would appear to be an unlikely contingency and the present results are best interpreted in the light of the similar transformations<sup>88</sup> recorded in the last Report (p. 99). In this case the oxidising agent was hydrogen peroxide in acetic acid, the occurrence of isomeric changes during the oxidation was shown to be a most unlikely event, and oleic and elaidic acids were regarded as *cis*- and *trans*-isomerides corresponding respectively to the dihydroxystearic acids of m. p. 94° and 137°. The formation and hydrolysis of the oxides of the two unsaturated acids may therefore be assumed to take place under the given conditions without the occurrence of isomeric changes. In connexion with the use of perbenzoic acid as oxidising agent it is recorded that when the double linking in an organic substance is conjugated with the carbonyl group it is not attacked by this acid or by peracetic acid. Thus ethyl fumarate and maleate yield only polymerides, whereas ethylenic substances are usually

<sup>84</sup> G. Florence, *Bull. Soc. chim.*, 1927, **41**, 440; *A.*, 540.

<sup>85</sup> H. W. Scheffers, *Rec. trav. chim.*, 1927, **46**, 293; *A.*, 645.

<sup>86</sup> S. H. Bertram, *ibid.*, p. 397; *A.*, 750.

<sup>87</sup> G. W. Pigulevski and M. A. Petrova, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1062; *A.*, 1927, 447.

<sup>88</sup> T. P. Hilditch, *J.*, 1926, 1828; *A.*, 1926, 938.

converted into the corresponding diols. The behaviour of diallyl is, however, abnormal, a furan derivative being apparently formed in place of the expected hexane- $\alpha\beta\epsilon\zeta$ -tetrol.<sup>89</sup>

A series of comparative experiments has been made on the catalytic hydrogenation of various *cis*- and *trans*-ethylenic compounds in alcoholic solution by means of hydrogen in the presence of palladous hydroxide. The results obtained with acids such as maleic, fumaric, oleic, elaidic, etc., and with their sodium salts indicate that the *cis*-compounds are uniformly more readily reduced than the corresponding *trans*-isomerides. A similar divergence is shown by the heats of combustion, those of the *cis*-compounds being the greater.<sup>90</sup>

Experiments on the oxidation of *isocerucic* acid by various reagents serve to show that the acid is an inseparable mixture containing approximately equal quantities of  $\Delta^{\lambda}$ -docosenecarboxylic acid and  $\Delta^{\nu}$ -docosenecarboxylic acid. The apparent homogeneity persists in certain of its derivatives, the methyl and the ethyl esters, the anilide, *p*-toluidide and the zinc salt all giving sharp melting points and simulating the behaviour of single substances.<sup>91</sup>

The synthesis of a number of polymethylene dicarboxylic acids of interest in connexion with muscone has been described. For example, from citronellal the ethyl ester of citronellideneacetic acid and citronellylacetic acid (30-dimethyl- $\Delta^7$ -decanoic acid) may in turn be obtained, and on ozonisation of the latter acid  $\gamma$ -methyl-hexane- $\alpha\zeta$ -dicarboxylic acid results. Variations of the procedure have led to the isolation of numerous  $\gamma$ -methyl dicarboxylic acids, which, unlike the corresponding  $\beta$ -methyl derivatives, are readily susceptible to racemisation in the presence of alkali.<sup>92</sup> The syntheses of  $\theta$ -,  $\iota$ -,  $\kappa$ -,  $\lambda$ -, and  $\mu$ -hydroxystearic acids<sup>93</sup> have been effected from  $\Delta^{\kappa}$ -undecenoyl bromide by proceeding *via* methyl  $\iota$ -aldehydo-decoate (obtained by converting the bromide successively into the nitrile and into  $\Delta^{\kappa}$ -dodecenoic acid, the methyl ester of which gives the required aldehydo-ester on ozonisation), and *via* methyl  $\kappa$ -aldehydoundecoate, which is obtained by acting on the bromide with ethyl sodiomalonate to give ethyl  $\Delta^{\kappa}$ -undecenylmalonate, followed by hydrolysis, elimination of carbon dioxide, esterification, and ozonisation of the methyl  $\Delta^{\lambda}$ -tridecenoate so formed. The aldehydo-esters are then treated with the appropriate Grignard reagent by the method of C. R. Noller and R. Adams.<sup>94</sup> Oxidation

<sup>89</sup> J. Böeseken, *Rec. trav. chim.*, 1926, **45**, 838; **A.**, 1927, 39.

<sup>90</sup> C. Paal and H. Schiedewitz, *Ber.*, 1927, **60**, 1221; **A.**, 646.

<sup>91</sup> T. J. Mirchandani and J. L. Simonsen, *J.*, 1927, 371; **A.**, 339.

<sup>92</sup> L. Ruzicka and R. Steger, *Helv. Chim. Acta*, 1927, **10**, 680; **A.**, 1170; L. Ruzicka and H. Stoll, *ibid.*, p. 691; **A.**, 1170.

<sup>93</sup> C. G. Tomecko and R. Adams, *J. Amer. Chem. Soc.*, 1927, **49**, 522; **A.**, 339.

<sup>94</sup> *Ibid.*, 1926, **48**, 1074; **A.**, 1926, 712.



of the aldehydo-acid obtained by ozonising  $\alpha$ -methyltridecenoic acid yields undecane- $\beta\lambda$ -dicarboxylic acid, which may also be obtained by the interaction of ethyl methylmalonate and methyl  $\iota$ -bromodecoate. For details of further numerous examples of monomethylated polymethylene dicarboxylic acids and their derivatives the reader is referred to the original paper.<sup>95</sup> Starting from undecenol,  $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_8\cdot\text{CH}_2\cdot\text{OH}$ , which can be made to give the  $\alpha$ -bromo- the  $\kappa$ -bromo- or the  $\alpha\kappa$ -dibromo-derivative by suitable treatment with hydrogen bromide, a lengthy series of compounds related to undecenoic acid and to *isoundecenoic acid*,  $\text{CHMe}\cdot\text{CH}\cdot[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$ , has been prepared.<sup>96</sup> Among these compounds is  $\iota$ -ketoundecenoic acid, which is obtained by oxidising the  $\alpha\kappa$ -diol prepared from  $\alpha\kappa$ -dibromo-undecane. This keto-acid has also been prepared from dehydro-undecenoic acid,  $\text{CH}\text{:C}[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$ , by treatment with mercuric acetate in acetic acid, followed by the action of hydrochloric acid on the mercuric  $\kappa\kappa\kappa$ -triacetoxymcuri- $\iota$ -ketoundecoate.<sup>97</sup>

The mercuration method has been applied to the preparation of several keto-acids. Thus  $\theta$ -ketostearic acid,  $\zeta$ -hydroxy- $\theta$ -ketostearic acid and  $\theta$ -ketobehenic acid are obtained respectively from stearolic, ricinoleic and behenolic acids.<sup>98</sup>

Undecenoic acid has been employed as the starting point in a synthesis of chaulmoogric acid. From  $\kappa$ -bromoundecenoic acid the corresponding cyano-derivative is prepared, and this is converted into the acid chloride of  $\kappa$ -cyanoundecenoic acid. This reacts with ethyl sodioacetoacetate to give a product whose sodium derivative is then treated with  $\Delta^2$ -cyclopentenyl chloride. Hydrolysis then results in the formation of *dl*- $\lambda$ -keto-chaulmoogric acid, which on reduction becomes *dl*-chaulmoogric acid, m. p.  $68.5^\circ$ . A noteworthy feature of the synthesis is that it involves at one stage the successful alkylation of a  $\beta\beta$ -diketonic acid.<sup>99</sup>

Cyclic ketones with large rings are known to be responsible for the musk aroma present in some animal products (see last Report, p. 188), and the similar odour of certain vegetable oils has now been traced to lactones of long-chain fatty acids.<sup>1</sup> After removal of the free fatty acids from musk-kernel oil, hydrolysis yields a mixture of palmitic and ambrettolic (*o*-hydroxy- $\Delta^5$ -hexadecenoic) acids, from

<sup>95</sup> P. Chuit, F. Boelsing, J. Hausser, and G. Malet, *Helv. Chim. Acta*, 1927, **10**, 167; **A.**, 446.

<sup>96</sup> *Idem, ibid.*, 1926, **9**, 1074; 1927, **10**, 113; **A.**, 1927, **40**, 445.

<sup>97</sup> W. W. Myddleton and A. W. Barrett, *J. Amer. Chem. Soc.*, 1927, **49**, 2258; **A.**, 1053.

<sup>98</sup> W. W. Myddleton, R. G. Berchem, and A. W. Barrett, *ibid.*, p. 2264; **A.**, 1053.

<sup>99</sup> G. A. Perkins and A. O. Cruz, *ibid.*, p. 1070; **A.**, 541.

<sup>1</sup> M. Kerschbaum, *Ber.*, 1927, **60**, 902; **A.**, 541.

which the small quantity of the latter may be isolated by fractional crystallisation. When kept, it gives rise slowly to an odoriferous lactone containing a large ring and to a lactide which is devoid of smell. The constitution of ambrettolic acid has been fixed by conversion of the acid into pimelic acid and azelaic acid by way of the ozonide. The lactone ambrettolide,  $\begin{matrix} \text{CH} \cdot [\text{CH}_2]_5 \cdot \text{CO} \\ | \\ \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CH}_2 \end{matrix} > \text{O}$ , b. p.

185—190°/16 mm., may be isolated directly from musk-kernel oil. Both it and its dihydro-derivative have a strong odour of musk, which is possessed also by the lactone of  $\zeta$ -hydroxypentadecic acid from angelica oil.

A study of the oil obtained by extracting the seed of English sheep's parsley (*Petroselinum sativum*) has been contributed.<sup>2</sup> Myristicin was identified as the chief constituent of the non-fatty portion, and after saponification the fatty acids consisted mainly of petroselic acid,  $\text{C}_{18}\text{H}_{34}\text{O}_2$ , together with some oleic, linoleic and palmitic acids. Petroselic acid yields lauric and adipic acids on oxidation with permanganate and gives a geometrical isomeride analogous to elaidic acid. The observations are in complete agreement with the formula  $\text{CH}_3 \cdot [\text{CH}_2]_{10} \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_4 \cdot \text{CO}_2\text{H}$  ascribed to petroselic acid by E. Vongerichten and A. Köhler.<sup>3</sup> A close resemblance thus exists between the composition of the English oil and that of the oil obtainable from Dutch parsley seed, of which also a full examination has been made. In the course of this the structure of petroselic acid was proved by ozonisation experiments, and in the second of the two papers referred to, the synthesis of the glyceride tripetroselin, identical with the natural product, is described.<sup>4</sup>

It has been found that diacetin and triacetin are converted into monoacetin when heated with excess of glycerol in the presence of phosphoric acid, and that a practically quantitative yield of monoacetin is obtainable when molar equivalents of glycerol and acetic acid are heated together in the presence of phosphoric acid or oxide at 170° for two hours.<sup>5</sup> The five margarins and the various mixed triglycerides containing margaric with palmitic or stearic acid residues have been prepared and examined,<sup>6</sup> the  $\alpha$ - and  $\beta$ -mono-margarins being obtained respectively by the methods of Fischer

<sup>2</sup> T. P. Hilditch and E. E. Jones, *J. Soc. Chem. Ind.*, 1927, **46**, 174; *A.*, 540.

<sup>3</sup> *Ber.*, 1909, **42**, 1638; *A.*, 1909, i, 454.

<sup>4</sup> J. van Loon, *Rec. trav. chim.*, 1927, **46**, 492; *A.*, 853; A. Steger and J. van Loon, *ibid.*, p. 703; *A.*, 1168.

<sup>5</sup> H. A. Schuette and P. P. T. Sah, *J. Amer. Chem. Soc.*, 1926, **48**, 3161; *A.*, 1927, 132.

<sup>6</sup> W. F. Thomson, *Trans. Roy. Soc. Canada*, 1926, iii, **20**, III, 445; *A.*, 1927, 540.

and Grün.<sup>7</sup> It is to be noted, however, that a recent examination of Grün's method has shown it to give  $\alpha$ -glycerides in place of the expected  $\beta$ -glycerides, and should this prove to be the usual course of the reaction, further inquiries will be necessary into the nature of the supposed  $\beta$ -margarin.<sup>8</sup>

An additional method for the preparation of glycerides and of esters in general lies in heating together the alcohol, the sodium salt of the fatty acid, and phosphorus pentachloride.<sup>9</sup> Esterification with ordinary alcohol in toluene in presence of hydrogen chloride as catalyst has also been described.<sup>10</sup> In the latter case the constant-boiling mixture of alcohol, toluene, and water is distilled, further additions of alcohol and toluene being then made until quantitative transformation to the ester has taken place.

Ethyl trifluoroacetoacetate may be prepared in the usual way by the interaction of ethyl acetate, ethyl trifluoroacetate and sodium ethoxide.<sup>11</sup> Evidence in favour of the formation of an addition compound of ethyl trifluoroacetate and sodium ethoxide was obtained and a study of the reaction mechanism has led this author to adopt Claisen's original explanation of the acetoacetic ester synthesis. The ester shows well-marked keto-enol tautomerism, the equilibrium mixture at 22° containing 66.2% of the enolic form. In the presence of water a stable keto-hydrate is produced which is transformed by sodium hydroxide into the enolic modification in an amount equivalent to the alkali added. Trifluoroacetoacetic acid, obtained from the ester by hydrolysis with hydrochloric acid, displays a remarkable stability and undergoes but slight decomposition when distilled at the ordinary pressure. It yields trifluoroacetone by the normal reaction when heated with sodium hydroxide.

A study of the addition of alkali alkyl oxides to esters<sup>12</sup> has shown that addition compounds are not formed with the esters of dibasic acids in which the groups are separated by more than one carbon atom. If, however, the linking  $-C:C-$  intervenes as in ethyl fumarate, reactivity is restored, and furthermore it is invariably possible with molecules of the type  $R \cdot CO \cdot CO \cdot R'$ , even when neither R nor R' is a carboxyl group. The experimental evidence in favour of the

<sup>7</sup> E. Fischer, M. Bergmann, and H. Barwind, *Ber.*, 1920, **53**, 1589; *A.*, 1920, **i**, 805; A. Grün, *Ber.*, 1910, **43**, 1288; *A.*, 1910, **i**, 356.

<sup>8</sup> A. Fairbourne and G. E. Foster, *J.*, 1926, 3148; *A.*, 1927, 131.

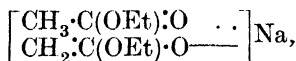
<sup>9</sup> R. K. Newman, V. M. Trikojus, and G. Harker, *Proc. Roy. Soc. New South Wales*, 1925, **59**, 293; *A.*, 1927, 40.

<sup>10</sup> R. Locquin and F. Elghozy, *Bull. Soc. chim.*, 1927, [iv], **41**, 445; *A.*, 543.

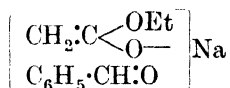
<sup>11</sup> F. Swarts, *Bull. Acad. roy. Belg.*, 1926, **12**, 679, 692, 721; *Bull. Soc. chim. Belg.*, 1926, **35**, 411; 1927, **36**, 313, 323; *A.*, 1927, 132, 646.

<sup>12</sup> F. Adiokes, *Ber.*, 1926, **59**, 2522; 1927, **60**, 272; *A.*, 1927, **41**, 228.

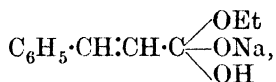
existence of an additive compound of ethyl acetate and sodium ethoxide is considered to be inadequate and reasons are given for doubting the constitution  $\text{COME}\cdot\text{CH}_2\cdot\text{C}(\text{OEt})_2\cdot\text{ONa}$  assigned by H. Scheibler and H. Ziegner<sup>13</sup> to the intermediate product in the acetoacetic ester synthesis. The constitution put forward by Scheibler<sup>14</sup> for the product derived from ethyl formate and sodium ethoxide is also challenged and evidence is given in support of the formula  $\text{CH}(\text{ONa})(\text{OEt})_2$ . In a later paper, H. Scheibler and E. Marhenkel<sup>15</sup> abandon the formula referred to above for the intermediate product in the acetoacetic ester synthesis and, whilst retaining the idea of an additive compound of ethyl acetate and sodium ethoxide, they now formulate the intermediate product as a quinhydrone-like sodio-derivative of ethyl acetate,



which when heated loses alcohol to form ethyl sodioacetoacetate, and which under other conditions may lead to the formation of the keten-acetal  $\text{CH}_2\cdot(\text{OEt})_2$ . With benzaldehyde, the ester present in the above complex in the keto-form is displaced to give



and this under suitable conditions rearranges to give



an intermediate product of the cinnamic ester synthesis. The new formula is applied to explain the characteristic reactions of the intermediate compounds, and substances of this type, formed either *via* a metallic ketyl or *via* an additive compound with sodium ethoxide or sodamide, etc., are postulated as playing an essential part in the condensation of two carbonyl groups. Reactions of such types as the Claisen condensation, the acetoacetic and the cinnamic ester condensations, and the aldol condensation are thus explicable. The observations of Adickes that only esters containing adjacent carbonyl groups form additive compounds with alkylloxides could not be confirmed by these authors.

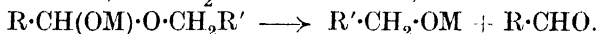
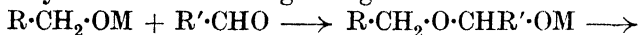
Similar problems are approached from another point of view in three papers on the combination of the carbonyl group in esters,

<sup>13</sup> *Ber.*, 1922, **55**, 789; *A.*, 1922, **i**, 426.

<sup>14</sup> *Ber.*, 1926, **59**, 1022; *A.*, 1926, 711. See also H. Scheibler, *Ber.*, 1927, **60**, 554; *A.*, 338.

<sup>15</sup> *Annalen*, 1927, **458**, 1; *A.*, 1167.

aldehydes, and ketones with metallic alkyl oxides.<sup>16</sup> Compounds of the type  $\text{CRR}'(\text{OM})\cdot\text{OR}''$ , for which the name metallic hemiacetal is proposed, are obtained when the carbonyl group in ketones, aldehydes, or esters combines with one molecule of metallic alkyl-oxide, aluminium and magnesium derivatives being especially considered in the communications now under review. Both the metallic and the corresponding free hemiacetals are largely dissociated in solution, and isolation in the pure condition is thereby rendered difficult, but evidence in support of the general formula is provided by the isolation of the ethylacetal of methyl nonyl ketone by the action of ethyl bromide on the product obtained from methyl nonyl ketone and sodium ethoxide. Of still greater theoretical interest is the formation from these acetals of products in which the functional groups of the original compounds have been interchanged. Thus in the combination of aldehyde and primary alkyl oxide the following change is observed :



The hemiacetal formed by the interchange dissociates into a new alkyl oxide and a new carbonyl compound, complete interchange being possible if the newly formed  $\text{R}\cdot\text{CHO}$  can be removed from the system. The observed behaviour suggests that these metallic compounds are capable of becoming ionised, the metal-containing ions giving reactions strictly parallel to those observed in inorganic chemical reactions. The theory of interchanges is developed to explain, amongst others, the Claisen-Titschenko reaction, the Cannizzaro reaction, the aldol condensation, and the formation of Fosseck's glycol,  $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ , from *isobutaldehyde* and potassium ethoxide. The explanation advanced for the Cannizzaro reaction is sketched in the following equations :  $\text{R}\cdot\text{CHO} + \text{NaOH} \longrightarrow \text{CHR}(\text{OH})\cdot\text{ONa} \longrightarrow$  (by loss of  $\text{NaOH}$  between two molecules)  $\text{CHR}(\text{OH})\cdot\text{O}\cdot\text{CHR}\cdot\text{ONa} \longrightarrow$  (by interchange)  $\text{CR}(\text{OH})(\text{ONa})\cdot\text{CH}_2\text{R} \longrightarrow \text{R}\cdot\text{CO}_2\text{Na} + \text{R}\cdot\text{CH}_2\cdot\text{OH}$ . Reactions of the type under discussion are of considerable practical interest in that they render possible the preparation not only of rare ketones and aldehydes, but also of otherwise inaccessible esters of tertiary or secondary alcohols. Thus geranyl anthranilate may be obtained from methyl anthranilate (1 mol.) and geraniol (1 mol.) by heating the two together in the presence of 0.05 mol. of sodium, aluminium or magnesium ethoxide. It will be obvious from this survey that many conflicting statements and ideas appear in the recent papers bearing on the mechanism of reactions in which the metallic alkyl-

<sup>16</sup> A. Verley, *Bull. Soc. chim.*, 1925, **37**, 537, 871; 1927, **41**, 788; *A.*, 1925, i, 783, 1034; *A.*, 1927, 856.

oxides play a prominent part, and the publication of further work must be awaited before it will be possible to make a final decision between the various competing formulæ.

Ethyl malonate, chloroform, and sodium ethoxide under carefully controlled conditions may be made to give good yields of ethyl sodiodicarbethoxyglutaconate, which with bromine gives ethyl  $\gamma$ -bromo- $\alpha\gamma$ -dicarbethoxyglutaconate. The latter with moist silver oxide in boiling alcohol yields ethyl allenetetracarboxylate,  $C(CO_2Et)_2:C:C(CO_2Et)_2$ , m. p.  $84^\circ$ . The ester is very sensitive to cold neutral permanganate, but reacts neither with bromine nor with hydrogen in the presence of palladised barium sulphate. Potassium ethoxide and ethyl  $\gamma$ -bromo- $\alpha\gamma$ -dicarbethoxyglutaconate gave rise unexpectedly to ethyl potassio- $\alpha\gamma$ -dicarbethoxyglutaconate and to ethyl  $\gamma$ -bromo- $\alpha\beta$ -diethoxy- $\alpha\gamma$ -dicarbethoxyglutarate, the latter of which could not be isolated but its presence was deduced from its decomposition products. Distillation of the original bromo-ester yields the lactone  $C_{13}H_{16}O_8$ , which gives with concentrated potassium ethoxide the salt,  $\begin{array}{c} CO \text{---} O \\ | \quad \quad \quad | \\ C(CO_2Et):CH \end{array} > C:C < \begin{array}{c} OK \\ OEt \end{array}$ , the lactone ring in which is stable towards potassium ethoxide.<sup>17</sup>

The addition of methyl sodiomalonate and of ethyl methylcyanoacetate to the butadiene esters methyl sorbate and methyl  $\beta$ -vinylacrylate occurs invariably in the  $\alpha\delta$ -positions, little or no trace of other additive products being formed.<sup>18</sup> Thus methyl  $\beta$ -vinylacrylate and methyl malonate yield exclusively methyl  $\Delta^7$ -pentene- $\alpha\alpha\epsilon$ -tricarboxylate, the double linking in which is now non-mobile and will neither suffer displacement by the action of sodium methoxide nor enable condensation with methyl cyanoacetate to be effected. In particular,  $\alpha\beta$ -products appear to be entirely absent and the scheme of 1:4- and 1:6-addition advocated by E. P. Kohler and F. R. Butler<sup>19</sup> is considered to be purely speculative.

### *Stereochemistry.*

The period under review has witnessed no essentially novel development of the subject, progress having taken place along lines already marked out or indicated by existing theory.

The general theory of K. Weissenberg,<sup>20</sup> in which attempt is made to formulate geometrical principles of stereochemistry leading to conceptions of the structure of carbon compounds which shall

<sup>17</sup> F. Faltis and J. Pirsch, *Ber.*, 1927, **60**, 1621; **A.**, 856.

<sup>18</sup> E. H. Farmer and A. T. Healy, *J.*, 1927, 1060; **A.**, 646.

<sup>19</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 1036; **A.**, 1926, 713.

<sup>20</sup> *Z. Krist.*, 1925, **62**, 13, 52; **A.**, 1926, 459; *Z. Elektrochem.*, 1926, **32**, 470; **A.**, 1927, 9; *Ber.*, 1926, **59**, 1526; **A.**, 1926, 934.

be in accord with the results of X-ray analysis [*e.g.*, for pentaerythritol,  $C(CH_2\cdot OH)_4$ , where the central carbon atom appears to have a pyramidal configuration], has received some attention. The theory postulates no fixed valency directions or lengths, the substituents arranging themselves around the carbon atom so that their potential energy is a minimum; every symmetrical arrangement corresponds to either a stable (energy minimum) or a labile (energy maximum) configuration; and only those symmetrical arrangements occur in which identical atoms occupy similar positions and different atoms dissimilar positions. Free rotation about the valency bonds cannot take place. Racemisation and the Walden inversion occur when the molecule is agitated so that the "energy peak" between two equally stable configurations is surmounted. The principles are intended to apply both to the solid and to the gaseous phase. According to W. Hückel,<sup>21</sup> the theory may possibly be of value in accounting for the existence of certain labile solid compounds (*e.g.*, the three *cis*-cinnamic acids) not anticipated from the chemical theory; but its extension to the gaseous phase, in which the number of isomerides is adequately accounted for on the classical principles, is unnecessary. It is pointed out by M. von Stackelberg<sup>22</sup> that the principles are difficult of theoretical application, and that the practical tests (*viz.*, the interpretation of X-ray measurements and the detection of labile solid isomerides at low temperatures) are at present undeveloped.

In this connexion, the isolation of three isomeric forms of phenyl  $\beta$ -methoxystyryl ketone,  $C_6H_5\cdot C(O\cdot CH_3)\cdot CH\cdot CO\cdot C_6H_5$ , by C. Dufraisse and A. Gillet,<sup>23</sup> is of interest, although it is suggested by J. A. Le Bel<sup>24</sup> that the existence of these compounds may be ascribed to the possibility of three equilibrium positions of the molecule under the mutual influences of the four dissimilar radicals. C. Weygand,<sup>25</sup> dealing with the same subject, mentions four forms of the corresponding ethoxy-compound, and also three forms of dibenzoylmethane,  $C_6H_5\cdot C(OH)\cdot CH\cdot CO\cdot C_6H_5$ . Curiously, the melting points of the three forms of dibenzoylmethane are identical with those of three of the forms of the ethoxy-derivative; and three of the forms of the latter melt at the same temperatures as three of the forms of the methoxy-compound. C. Weygand and H. Forkel<sup>26</sup> report the isolation of colourless and yellow sodium salts of benzoylacetone. Of these forms, which are interconvertible,

<sup>21</sup> *Ber.*, 1926, **59**, 2826; *A.*, 1927, 129.

<sup>22</sup> *Z. angew. Chem.*, 1927, **40**, 1023; *A.*, 1911.

<sup>23</sup> *Compt. rend.*, 1926, **183**, 746; *A.*, 1927, 58.

<sup>24</sup> *Ibid.*, p. 889; *A.*, 1927, 38.

<sup>25</sup> *Ber.*, 1927, **60**, 2430.

<sup>26</sup> *J. pr. Chem.*, 1927, **116**, 293; *A.*, 971.

the yellow is soluble in water but not in benzene, and the other is soluble in benzene.

A less accountable case of isomerism is found in the report<sup>27</sup> (which, however, awaits confirmation) that 3-chloro-1-bromo-4 : 6-dinitrobenzene exists in two isomeric forms having the same melting point, the one substance resulting from 3-chloro-4 : 6-dinitroaniline and the other from the corresponding bromo-compound. Should this observation be substantiated, it would imply a stabilisation of the Kekulé phases of the benzene nucleus under the influence of certain substituents; but it is well known that previous reports of the occurrence of this type of isomerism have proved ill-founded.

J. K. Senior<sup>28</sup> has worked out expressions giving the number and nature of the isomerides to be expected in compounds of the types *Caxyz*, *Cxyzv*, and *Nxyz*, where *a* is a symmetrical, saturated, non-cyclic substituent and *x*, *y*, *z*, *v* are four structurally different, non-cyclic substituents containing different numbers of asymmetric carbon atoms; cases are also given in which *y* = *x*, etc.

*Long-chain Series.*—The question of the configurations assumed by the normal fatty acids, as deduced from X-ray evidence (see *Ann. Reports*, 1923, 20, 242), is further complicated by observations, such as that of G. M. de Boer,<sup>29</sup> that the long spacing given by stearic acid obtained by slow crystallisation differs from that afforded by a thin layer of the acid obtained by fusion or evaporation, the existence of modifications of stearic acid with carbon chains of different lengths being thus indicated. Similar observations had already been made by S. H. Piper, T. Malkin, and H. E. Austin,<sup>30</sup> who found that the higher fatty acids, generally, have at least two forms of chain, and palmitic and stearic acids have three possible forms. The alternative spacings, unlike those of the normal paraffins, are independent of the temperature, but are dependent on the previous history of the specimen. The crystal spacings are considerably affected by the presence of impurities.<sup>31</sup>

It was already clear from general stereochemical theory that in a normal chain series,  $R \cdot [CH_2]_n \cdot R'$ , where *R* and *R'* are symmetrical groupings, the methylene groups must be oriented successively in a *cis*- and *trans*-manner in order to preserve the symmetry of the molecule (regarded as static) after the first few members; but it had been tacitly assumed that the absence of manifestation of molecular dissymmetry among such compounds was attributable

<sup>27</sup> H. H. Hodgson, *J. Soc. Dyers and Col.*, 1926, 42, 365; *A.*, 1927, 47.

<sup>28</sup> *Ber.*, 1927, 60, 73; *A.*, 226.

<sup>29</sup> *Nature*, 1927, 119, 50; *A.*, 98.

<sup>30</sup> *J.*, 1926, 2310; *A.*, 1926, 1083.

<sup>31</sup> See also J. Thibaud, *Compt. rend.*, 1927, 184, 24; *A.*, 98.



to the occurrence of free rotation about the bonds forming the chain. It is now suggested by B. Nekrassov<sup>32</sup> that an assumption of the semi-permanence of this symmetrical zigzag configuration may serve to account for the existence of the well-known "odd and even" sets of members of such series, the end groups in one set being relatively *cis*- and in the other *trans*-, occasioning thereby a phenomenon resembling geometrical isomerism. Evidence in support of this view is adduced from a comparison of melting point, solubility, dielectric constant, surface tension, molecular volume, and other physical properties of the members of odd and even series; and it is shown that, with increase of temperature, the differentiation between the two series tends to disappear, owing to diminution of the resistance of the chains to free rotation. The oscillation of the melting point of the *cycloparaffins* is explained by assuming that rotation must occur when a chain of an odd number of carbon atoms closes, but not necessarily with the closure of a chain of an even number. Current theory, however, would seem to require the rotation of the alternate atoms of the chain in both cases (except, perhaps, in the case of large rings in which the carbon atoms are not finally in one plane), since the zigzag (*cis*- and *trans*-) chain cannot be preserved in a ring.

The oscillation of the melting point in "odd and even" series, already demonstrated<sup>33</sup> among the amides of the monobasic acids, has now been shown to hold for the amides and substituted amides of the dibasic acids.<sup>34</sup> The phenomenon, which is manifested even in such series as the *cyclotelluropentanediones*,<sup>35</sup> is therefore apparently a very general<sup>36</sup> one.

$\alpha\beta$ -Distearin has been converted, by means of chlorosulphonic acid, into  $\alpha\beta$ -distearin hydrogen sulphate, and the latter into the strychnine salt, which has been separated into diastereoisomerides by fractional crystallisation.<sup>37</sup> The potassium salts of the *d*- and *l*- $\alpha\beta$ -distearin sulphates are found to be practically inactive in solvents at temperatures above 40°, but, when the solutions are cooled below 35° so that they become colloidal, the initial small specific rotation is reversed in sign and then increases with time to a very high maximum. The change is reversible. The potassium salts of the corresponding phosphates behave in a similar but less marked manner.

<sup>32</sup> *Z. physikal. Chem.*, 1927, **128**, 203; **A.**, 922.

<sup>33</sup> P. W. Robertson, *J.*, 1908, **93**, 1033; 1919, **115**, 1210.

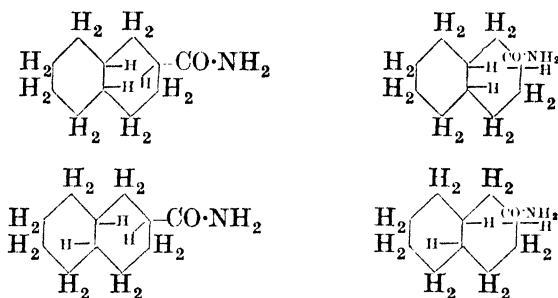
<sup>34</sup> C. R. Barnicoat, *J.*, 1927, 2926.

<sup>35</sup> G. T. Morgan and H. D. K. Drew, *J.*, 1924, **125**, 736.

<sup>36</sup> Compare O. Biach, *Z. Physik*, 1904, **50**, 43.

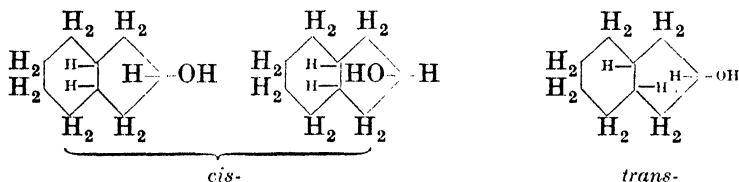
<sup>37</sup> A. Grün and R. Limpächer, *Ber.*, 1927, **60**, 255; **A.**, 226.

"*Strainless*" Rings.—A number of further examples illustrating the *cis*- and *trans*-fusion of saturated ring systems have recently been brought to light. In the decahydronaphthalene series, F. W. Kay and N. Stewart<sup>38</sup> have isolated a new decahydro- $\beta$ -naphthoamide (m. p. 139–140°), making, with the two isomerides<sup>39</sup> already known (m. p.'s 165–166° and 195°, respectively), three of the four theoretically possible (racemic) forms :



and W. Hückel and his collaborators<sup>40</sup> have completed the isolation of four isomerides (in each case) of  $\beta$ -hydroxy- and  $\beta$ -amino-decahydronaphthalene.

In the hexahydrohydrindene series, W. Hückel and H. Friedrich<sup>41</sup> have obtained the two theoretically indicated *meso*-forms, together with the remaining possible form (*trans*- and presumably racemic) of hexahydro- $\beta$ -hydrindol :



Among ring systems containing nitrogen, hydrogenation of quinoline in presence of colloidal platinum has given rise, in addition to the known (*trans*-) decahydroquinoline, to a new (*cis*-) isomeride.<sup>42</sup> For reductions carried out in presence of acetic acid containing hydrochloric acid, the product contains 65% of the new isomeride ;

<sup>38</sup> *J.*, 1926, 3038; *A.*, 1927, 147.

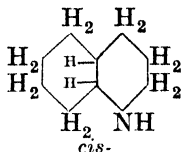
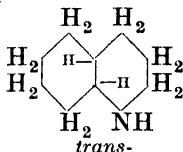
<sup>39</sup> W. Borsche and E. Lange, *Annalen*, 1923, **434**, 219; *A.*, 1924, i, 32.

<sup>40</sup> W. Hückel, R. Mentzel, E. Brinkmann, and E. Kamenz, *ibid.*, 1926, **451**, 109; *A.*, 1927, 238.

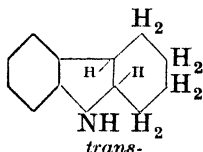
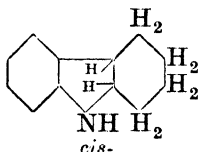
<sup>41</sup> *Ibid.*, p. 132; *A.*, 1927, 238.

<sup>42</sup> W. Hückel and F. Stepi, *ibid.*, 1927, **453**, 163; *A.*, 572.

whereas only 10% is produced by reduction of the oxalate in aqueous solution (the remainder is the *trans*-compound in each case) :



Similarly, by the reduction of tetrahydrocarbazole with tin and hydrochloric acid, J. Gurney, W. H. Perkin, jun., and S. G. P. Plant<sup>43</sup> have isolated, in small yield (1—2%), a second form of hexahydrocarbazole, which they regard as the *trans*-form :



Each of the four nitrogenous ring compounds should theoretically be resolvable.

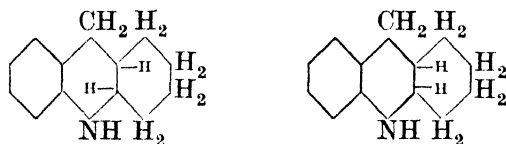
These and previously discovered examples provide a sound basis for the hypothesis that two saturated rings may become fused both in the *cis*- and in the *trans*-positions ; and it follows from general theory that the two rings forming the resulting dicyclic compound cannot be in the same plane in either case. Beyond this, however, the number and type of the stereoisomerides hitherto isolated in a given instance appear to yield of themselves no information as to the stereochemical nature of the rings. Thus it hardly seems justifiable to cite the results as a verification of the predictions of the Sachse theory as applied by Mohr. It will be remembered that Sachse proposed two forms of the strainless *cyclohexane* ring, neither of which is uniplanar with respect to the carbon frame : the one form (A) is generated by joining the vertices of the carbon tetrahedra so that the corners of the triangular base of each succeeding tetrahedron, when projected, lie over the mid-points of the sides of the foregoing base ; and the other form (B) is made up of two pairs of tetrahedra, united in the normal way, but separated by two single tetrahedra placed in relatively *para*-positions in the manner of the first model. Neither model, regarded as a fixed form, can represent *cyclohexane* or its substituted derivatives, since, on the one hand, non-existent isomerides would be predicted, and, on the other, the data obtained from *X-ray* examination<sup>44</sup> of benzene hexahalides (the  $\beta$ -forms) are in disagreement with such

<sup>43</sup> *J.*, 1927, 2676.

<sup>44</sup> S. B. Hendricks and C. Bilicke, *J. Amer. Chem. Soc.*, 1926, **48**, 3007 ; *A.*, 1927, 98.

a conclusion. In Mohr's decahydronaphthalene model (*J. pr. Chem.*, 1918, [ii], **98**, 315) the *cis*-form is built up from two Sachse B forms, in which the exceptional *para*-carbon atoms are retained; and the *trans*-form is made by the union of two Sachse A forms. Thus it is postulated that, if the uniplanar ring for *cyclohexane* is retained, three distinct forms of the saturated six-membered ring are represented among *cyclohexane* and the two decahydronaphthalenes. On the other hand, if the decahydronaphthalene molecule be regarded as being built up by the fusion of two uniplanar *cyclohexane* rings, then, whereas the resulting *cis*-form is free from abnormal strain, the corresponding *trans*-form is seen to be considerably (though perhaps not unbelievably) strained. In the absence, therefore, of decisive evidence derived from measurement of the heats of combustion<sup>45</sup> of *cis*- and *trans*-forms, it seems not impossible to retain the view that the dicyclic systems are made up of inclined uniplanar rings. In any case, the numbers of multipplanar isomerides predictable on this and on the Sachse-Mohr hypothesis are identical, so that consideration of them is valueless as a test between the two theories. Whichever is correct, it seems clear, so far as evidence goes at present, that the two rings from which either form of the decahydronaphthalene molecule is built up are structurally similar.

In connexion with the optical stability of such systems, an interesting question has been raised by Hückel and Stepf (*loc. cit.*, p. 171). They point out that the optically active octahydroacridines of W. H. Perkin, jun., and W. G. Sedgwick,<sup>46</sup> all four of which were prepared, have been shown by their discoverers to be racemised either by distillation or by treatment (in the case of one



*cis*- and *trans*-Octahydroacridines (racemic forms).

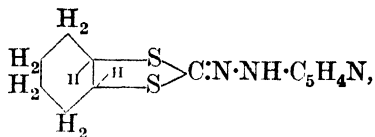
of them) with acetic anhydride. In the opinion of Hückel and Stepf this behaviour throws doubt upon the relationship of the compounds, because it implies that change of configuration may take place at both asymmetric carbon atoms, but not at one alone—for this would involve the transformation of a *cis*- into a *trans*-form (or *vice versa*) which does not occur.

It should be noted that the pyridylhydrazone of *cyclohexylene* dithiocarbonate (W. H. Mills and H. Schindler, *J.*, 1923, **123**, 312)

<sup>45</sup> Compare W. Hückel, *Annalen*, 1927, **455**, 123; **A.**, 773.

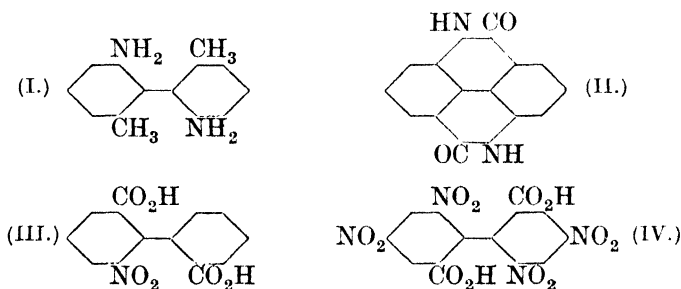
<sup>46</sup> *J.*, 1924, **125**, 2437; 1926, 438.

is now, in view of the foregoing developments, considered by Mills<sup>53</sup> to possess the *trans*-formula :



so that its resolution should no longer be regarded as any indication of the tetrahedral distribution of valencies in the doubly-linked nitrogen atom—although, of course, the proof of this distribution in other cases remains unaffected.

*The Diphenyl Series.*—Recent work in the diphenyl series tends strongly to confirm the “obstacle” theory of Bell and Kenyon, which explains the occurrence of optically active forms among nitro- and chloro- (6- and 6'-) substituted diphenic (2- and 2'-) acids on the assumption that two groups (in the 2- and 6-positions) may restrict the rotation of the opposite ring by impinging upon the group or groups in the 2'- and 6'-positions, thus preventing the rings from becoming co-planar. J. Meisenheimer<sup>47</sup> has resolved 6 : 6'-diamino-di-*o*-tolyl (I) by means of *d*- and *l*-tartaric acids, thus showing that resolvability is not dependent upon the presence of carboxy-groups. The active bases are optically stable. Their



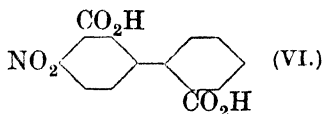
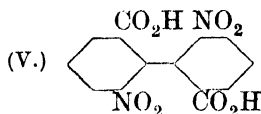
acetyl derivatives have been oxidised to the corresponding diacetamidodiphenic acid, and the acetyl groups have been removed from the active enantiomorphs of this acid by means of sulphuric acid at the ordinary temperature. The resulting dilactam (II) was completely inactive, as would be anticipated from the theory—since the closing of the lactam rings would bring the phenyl rings into a common plane, whilst the valencies to tervalent nitrogen are at the same time uniplanar. The acid (III) is<sup>48, 49</sup> very much less optically stable than (IV); and (V) is now shown<sup>49</sup> to be optically

<sup>47</sup> *Ber.*, 1927, **60**, 1425; **A.**, 766.

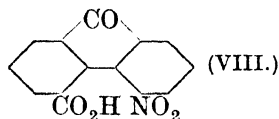
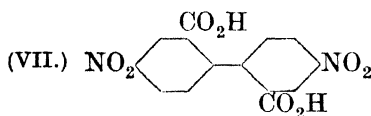
<sup>48</sup> F. Bell and P. H. Robinson, *J.*, 1927, 2234; **A.**, 1069.

<sup>49</sup> R. Kuhn and O. Albrecht, *Annalen*, 1927, **455**, 272; **A.**, 876.

stable to sulphuric acid at 98°, or, in the form of its sodium salt, to water at 140—160°. The resistance offered to annular revolution by the hindering substituents is very considerable, and is much greater for four groups than for three.



The obstacle-free acid (VI) has resisted resolution,<sup>50</sup> whereas the active form of (VII) is immediately racemised<sup>51</sup> on liberation from its alkaloidal salts. All these facts are in accord with the theory,



except that (VI) might have been expected to exhibit behaviour similar to that of (VII).

An important aspect of the general problem is opened by the observation, first made by G. H. Christie and J. Kenner,<sup>52</sup> and recently in more detail by F. Kuhn and O. Albrecht,<sup>51</sup> that the obstacle-free acid (VII) undergoes asymmetric transformation when combined with alkaloids (quinine, cinchonidine), *i.e.*, is transformed almost completely to the salt of one enantiomorph, whereas the acids possessing at least three obstructing groups (*e.g.*, IV) yield both diastereoisomeric alkaloidal salts. If we imagine the rings in an active acid such as (VII) to be, let us say, perpendicular to one another, a rotation of one of them through 180° with respect to the other, about the common axis, will transform the acid to its enantiomorph. Such a rotation can occur in (VII) even if the two carboxy-groups cannot pass each other, but it will be unable to occur in (IV) if neither a nitro-group nor a carboxyl can pass another of such groups. It follows, therefore, that (VII) will be capable both of asymmetric transformation and of racemisation, whereas (IV) will be capable of neither; but at the same time it is indicated that the presence of the obstacle groups, as such, is not the cause of the resolvability, but only the means of preserving dissymmetry when it has become established. This consideration suggests that diphenyl compounds containing only one substituent in each of the 3- and 3'-positions might be capable of asymmetric transformation under the influence of an alkaloid; and such a speculation

<sup>50</sup> F. Bell and P. H. Robinson, *J.*, 1927, 1695; **A.**, 876.

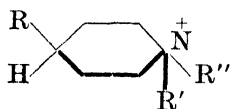
<sup>51</sup> F. Kuhn and O. Albrecht, *loc. cit.*

<sup>52</sup> *J.*, 1922, **121**, 616.

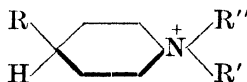
raises anew the question as to how asymmetric reagents, such as alkaloids, are capable of inducing the molecules with which they are combined to assume fresh space-forms. The study of the diphenyl series promises to throw much light on the obscure phenomena connected with the free rotation of groups.

It may be noted that 5-nitrofluorenone-4-carboxylic acid (VIII) is non-resolvable,<sup>48</sup> which indicates the co-planar disposition of the three rings comprising the fluorenone molecule.

*Stereoisomerism among Ionised Compounds.*—(1) *The ammonium ion.* W. H. Mills and his collaborators have brought forward further evidence in favour of the tetrahedral, as opposed to the pyramidal, configuration of the ammonium ion. They had previously demonstrated the resolvability of 4-phenyl-4'-carbethoxy-bispiperidinium-1 : 1'-spiran bromide (see *Ann. Reports*, 1926, **23**, 102) in which a pyramidal configuration would be symmetrical; and they now show<sup>53</sup> that isomerism among salts of the general formula,  $R\text{-CH}\left\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\right\rangle\text{NR}'\text{R}''\text{X}$ , prepared from 4-phenylpiperidine and 4-hydroxypiperidine, is in accordance with the tetrahedral configuration of the quaternary nitrogen atom but not with the pyramidal. Where R' and R'' are different, the tetrahedral configuration predicts the occurrence of two (*cis*- and *trans*-) non-resolvable isomerides, which become identical if R' = R''. The pyramidal configuration, on the other hand, requires two racemic compounds, when R' and R'' are different, these becoming simple (*cis*- and *trans*-) non-resolvable forms if R' = R'' :



Pyramidal



Tetrahedral

(*trans*-forms, with respect to R and R')

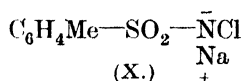
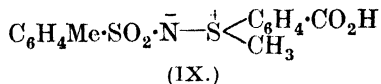
Actually, for eight salts in which R' and R'' were different (*e.g.*, 4-phenyl-1-methyl-1-ethylpiperidinium iodide), two geometrical isomerides were found in each case; and, for two salts in which R' and R'' were identical (*e.g.*, 4-phenyl-1 : 1-diethylpiperidinium iodide) the substances proved to be homogeneous in each case.

(2) *Resolution of a sulphonylimine.* The condensation of chloramine-T with *m*-carboxyphenyl methyl sulphide gives a sulphilimine which is resolvable<sup>54</sup> into *l*- and *d*-forms by the use of brucine and cinchonidine. Since the trivalent nitrogen atom cannot here be

<sup>53</sup> W. H. Mills, J. D. Parkin, and W. J. V. Ward, *J.*, 1927, 2613; **A.**, 1199.

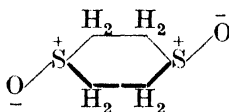
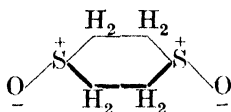
<sup>54</sup> S. G. Clarke, J. Kenyon, and H. Phillips, *ibid.*, p. 188; **A.**, 243.

otherwise than symmetrical if the double bond is non-polar, the sulphur atom must be regarded as linked to the nitrogen by a semi-polar double bond, just as sulphur is joined to oxygen in the (resolvable) sulphinates and sulfoxides. The compound must therefore



possess the formula (IX), in which the sulphur atom may be regarded as situated at one corner of an empty tetrahedron. Chloramine-T itself is represented by the formula (X).

(3) *Isomerism of disulphoxides*. Since the sulfoxides have been shown to possess a semi-polar double bond, it follows that disulphoxides should show geometrical isomerism. A second form of the disulphoxide of 1 : 4-dithian has now been isolated,<sup>55</sup> these compounds being representable by the *cis*- and *trans*-forms :



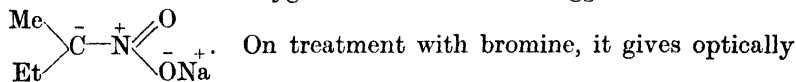
Dimethyldithiolethane disulphoxide,  $\text{MeS(O)}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S(O)Me}$ , exists also in  $\alpha$ - and  $\beta$ -forms. Of greater interest is the suggestion that the isomeric forms of thianthren disulphoxide (Fries and Vogt, *Ber.*, 1911, **44**, 756) owe their existence to a similar development of dipoles.

(4) *Optically active sodium aci- $\beta$ -nitrobutane*. R. Kuhn and H. Albrecht,<sup>56</sup> by acting upon active *sec*-butyl iodide with silver nitrite at  $0^\circ$ , separating the resulting active  $\beta$ -nitrobutane, and treating it with methyl-alcoholic sodium methoxide, have isolated the optically active sodium salt of *aci*- $\beta$ -nitrobutane. If this remark-

able substance were representable by the formula

$$\begin{matrix} \text{Me} \\ \diagdown \\ \text{C}=\text{N}^+ \\ \diagup \\ \text{Et} \end{matrix} \begin{matrix} \diagup \bar{\text{O}} \\ \diagdown \text{ONa}^+ \end{matrix}$$

it would not exhibit dissymmetry even if the sodium atom remained in attachment to oxygen. The authors suggest the formula



active  $\beta$ -bromo- $\beta$ -nitrobutane. The change of a nitro-compound into its *aci*-form represents thus the intramolecular displacement of a semi-polar double bond.

(5) *Optically active aluminium compounds*. Ammonium alumin-

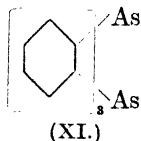
<sup>55</sup> E. V. Bell and G. M. Bennett, *J.*, 1927, 1798; **A.**, 958.

<sup>56</sup> *Ber.*, 1927, **60**, 1297; **A.**, 749.



trioxalate has been obtained <sup>57</sup> in an active condition by conversion into the strychnine salts, separation by fractional extraction with water, and reconversion of the fractions to ammonium salts,  $[\text{Al}(\text{C}_2\text{O}_4)_3](\text{NH}_4)_3$ . The salts are autoracemised in aqueous solution. Aluminium is the twentieth element shown to give rise to optical activity.

A compound representing a new space-type has been prepared by N. P. McClelland and J. B. Whitworth.<sup>58</sup> It is a crystalline substance, tri-*o*-phenylenediarsine (XI), in which a pair of arsenic atoms is united to three benzene rings in the ortho-position so that the planes of the rings, if symmetrically disposed, are inclined at  $120^\circ$  to one another, the arsenic atoms (which are not joined together) being in the axis of the solid figure. The stereochemistry of the nuclear derivatives of this substance should prove of exceptional interest.



An observation <sup>59</sup> which may have a bearing upon the natural synthesis of optically active substances is to the effect that certain aromatic monoketones and aliphatic  $\alpha$ -diketones, which behave as photocatalysts in the oxidation of alcohols to aldehydes, may be used, in presence of an optically active substance, to effect a preferential change in one of a pair of optical antipodes. Racemic methylethylcarbinol, containing *l*-menthyl benzophenone-*p*-carboxylate, yielded the levorotatory alcohol after exposure to light in presence of oxygen.

The question whether the groups in 4-co-ordinated complex salts, such as those of cobalt, nickel, platinum, and palladium, are in general tetrahedrally disposed or have the plane configuration is still largely open. H. Reihlen <sup>60</sup> considers the evidence to favour a tetrahedral configuration, but A. Grünberg <sup>61</sup> attempts to show that the arrangement of the groups in the platinous salts is influenced by their electrochemical nature, the data favouring to varying extents a plane, pyramidal, or a tetrahedral configuration. F. Krauss and F. Brodkorb <sup>62</sup> show that a plane configuration satisfies the isomerism of the yellow and the red palladous salts,  $\text{PdCl}_2(\text{NH}_3)_2$ ,  $\text{PdCl}_2(\text{NH}_2\text{Et})_2$ , and  $\text{PdCl}_2(\text{C}_5\text{H}_5\text{N})_2$ . F. G. Mann <sup>63</sup> has examined

<sup>57</sup> W. Wahl and M. Andersin, *Ber.*, 1927, **60**, 399; **A.**, 339.

<sup>58</sup> *J.*, 1927, 2753.

<sup>59</sup> J. Böeseken and S. L. Langedijk, *Proc. K. Akad. Wetensch. Amsterdam*, 1927, **30**, 189; **A.**, 739.

<sup>60</sup> *Annalen*, 1926, **448**, 316. Compare H. Reihlen and K. T. Nestle, *ibid.*, 1926, **447**, 211; *Z. anorg. Chem.*, 1927, **159**, 343.

<sup>61</sup> *Z. anorg. Chem.*, 1927, **164**, 207; **A.**, 922.

<sup>62</sup> *Ibid.*, **165**, 73; **A.**, 951.

<sup>63</sup> *J.*, 1927, 2904.

several new nickelous salts from this point of view, without, however, arriving at a decision. Instances of tetrahedral 4-co-ordinated salts of copper, zinc, and beryllium (Mills and Gotts) are already known; but, on the other hand, the work of Vernon suggested plane formulæ for the isomeric dimethyltelluronium dihalides (not strictly analogous to the salts mentioned above), although the members of the two series here differ remarkably in colour and physiological activity. There is clearly a possibility that the structural nature of the 4-co-ordinated compounds may prove less uniform than is at present assumed.

The revival of Stark and Thomson's conception of the single-electron ("singlet") linkage, as a result of S. Sugden's measurements<sup>64</sup> of the parachors of phosphorus and antimony pentachlorides, may have important consequences for stereochemical theory. For example, three of the chlorine atoms in phosphorus pentachloride are linked by co-valencies, whereas the last two are indicated as attached each by a single electron. The theory, however, is at present too little developed for discussion. Reference may be made on this point to Dr. N. V. Sidgwick's<sup>65</sup> book on the electronic theory of valency which has appeared during the year.

Uniaxial optically active crystals of the following substances have been examined<sup>66</sup> by the X-ray method: *d*-potassium rhodium oxalate,  $[\text{Rh}(\text{C}_2\text{O}_4)_3]\text{K}_3 \cdot \text{H}_2\text{O}$ ; sodium periodate,  $\text{NaIO}_4 \cdot 3\text{H}_2\text{O}$ ; ethylenediamine sulphate,  $\text{C}_2\text{H}_4(\text{NH}_2)_2 \cdot \text{H}_2\text{SO}_4$ ; and guanidine carbonate,  $(\text{CN}_3\text{H}_5)_2 \cdot \text{H}_2\text{CO}_3$ . The rotatory power of the crystals is held to be due to some definite arrangement of atoms within a unit of structure, and not to a spiral arrangement of biaxial lamellæ. In *d*-potassium rhodium oxalate the molecules occupy a spiral arrangement in the crystal.

In the compilation of this Division of the Report the undersigned has had the valuable help of Dr. H. D. K. Drew and of Dr. E. L. Hirst, and their assistance is here gratefully acknowledged.

W. N. HAWORTH.

<sup>64</sup> *J.*, 1927, 1173; *A.*, 714.

<sup>65</sup> "The Electronic Theory of Valency" (Clarendon Press, 1927).

<sup>66</sup> W. G. Burgers, *Proc. Roy. Soc.*, 1927, *A*, 116, 553; *A.*, 1126.

## PART II.—HOMOCYCLIC DIVISION.

*Tautomerism.*

DURING the present year much attention has been concentrated on certain parts of this subject, which was not dealt with in the last Report.

(1) *Mobile Cation Tautomerism (Cationotropy). Special Case: Prototropy; Pseudo-acidity.*<sup>1</sup>—It is recognised that the condition for the occurrence of mobile cation tautomerism is that an atom (*e.g.*, hydrogen or a metal) should become detached from an unsaturated molecule, leaving an electromeric anion which, in the simplest case, is of the form  $x-y\overset{\ominus}{=z}$ ; tautomeric electron displacements, such as  $x\overset{\curvearrowright}{\rightleftharpoons}y\overset{\curvearrowright}{\rightleftharpoons}z$ , then bring about a distribution (both in time and space) of the negative charge between *x* and *z*, so that the eliminated cation has two possible points of recombination. One consequence of this view is that mobile hydrogen and mobile metals are in the same category, their apparently large differences of behaviour (*e.g.*, in  $\beta$ -diketones and nitromethanes and their salts) being attributable to the very different degrees of stability of their covalency unions;<sup>2</sup> thus arise the characteristic phenomena of pseudo-acidity. Another consequence is that the tendency of a tautomeric system to come into equilibrium under given conditions (the mobility of the system) will depend fundamentally on the stability, under those conditions, of the organic anion in which the real structural change occurs; hence the importance of alkaline catalysis. A third result is that the equilibrium attained, since it involves the changes  $A \rightleftharpoons H^+ + A' \rightleftharpoons B' + H^+ \rightleftharpoons B$ , will depend jointly on the relative stabilities of the two anions ( $A' \rightleftharpoons B'$ ) and on the relative stabilities of the covalent links by means of which the common cation associates with each of them.

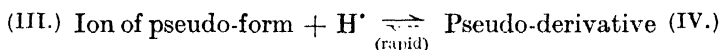
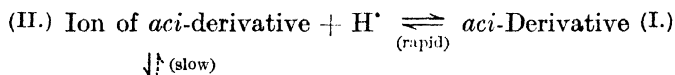
Some of these conclusions are strikingly illustrated by the study of nitromethane derivatives, two important investigations on which

<sup>1</sup> The nomenclature and arrangement of this section are self-explanatory and are those used by the Reporter on the occasion of the meeting of Section B of the British Association on August 9th, 1926, in Oxford.

The term "electromerism" (= mobile electron tautomerism) was introduced by H. S. Fry ("The Electronic Conception of Valence," 1921), and the term prototropy (= mobile hydrogen, or mobile proton, tautomerism) by T. M. Lowry (*J.*, 1923, **123**, 828). Lowry has also used the word "ionotropy" (Report of the Second Solvay Conference, 1925, p. 182), from which "cationotropy" and "anionotropy" have been derived.

<sup>2</sup> W. A. Noyes (*Proc. Nat. Acad. Sci.*, 1927, **13**, 379; *A.*, 814) has explained this in a manner closely related to K. Fajan's general theory of covalency formation (*Naturwiss.*, 1923, **11**, 105; *A.*, 1923, ii, 750).

have been published during the year. The anion of phenylnitromethane is stable in alkaline aqueous solution (that is, in the practical absence of cations, such as hydrion, having a strong tendency to form covalency unions) and Hantzsch showed that its association with hydrion could be followed by conductivity measurements. This reaction has now been subjected to a detailed analysis.<sup>3</sup> When a dilute aqueous methyl-alcoholic solution of the sodium salt of phenylisnitromethane is mixed with an equivalent amount of hydrochloric acid, the conductivity falls in such a way as to show that after an initial disturbance, due to the rapid formation of a comparatively weak electrolyte in equilibrium with its ions, one of these ions becomes involved in a slow unimolecular change resulting ultimately in the complete production of the undissociated  $\psi$ -acid. Other nitro-compounds, including *p*-nitrophenol, behave in a similar way. On the view that the slow change is that which involves the alteration of structure, the general conclusions may be thus expressed :



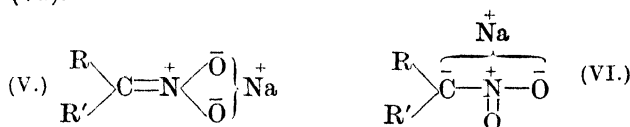
The comparatively weak electrolyte is obviously to be identified with the *aci*-derivative (I), and an important feature of the work is the proof that it is not the molecule of this compound but its ion which undergoes the slow unimolecular change. (It was possible to show this because the concentrations of I and II do not bear a constant relation to each other : as the *aci*-compound is destroyed, so the fraction ionised increases.) The reaction (II)  $\longrightarrow$  (III), which can be reversed under other conditions, is in this case not measurably reversible, because it is succeeded by the rapid and substantially complete ionic association (III)  $\longrightarrow$  (IV). It is the stability of the covalent C-H link formed in the last reaction, in contrast with the ready ionisability of the O-H link produced in reaction (II)  $\longrightarrow$  (I), which determines the whole series of changes in the general direction (I)  $\longrightarrow$  (IV). Evidence of the existence of the ion of the pseudo-form comes from another source.<sup>4</sup> It has been shown that optically active  $\beta$ -nitrobutane yields an optically active sodium salt, which on treatment with bromine gives an optically active  $\beta$ -bromo- $\beta$ -nitrobutane :



<sup>3</sup> G. E. K. Branch and J. Jaxon-Deelman, *J. Amer. Chem. Soc.*, 1927, **49**, 1765; **A.**, 852.

<sup>4</sup> R. Kuhn and H. Albrecht, *Ber.*, 1927, **60**, [B], 1297; **A.**, 749.

This cannot be held to obliterate the mass of evidence in favour of the existence of the *aci*-nitro-anion (as in V), but it will be agreed that it appears to necessitate the recognition of a pseudo-nitro-anion also (VI).<sup>5</sup>

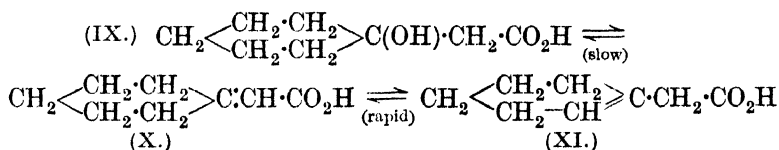


If this is so, it destroys the commonly encountered dogma that in ethyl sodioacetoacetate and similar derivatives the metal (that is to say, the anionic charge) must necessarily be attached exclusively to oxygen.

Further evidence regarding the general mechanism of prototropic change emerges from the study of examples in which a considerable concentration of alkali (usually hydroxide or ethoxide ions) is required to effect reversible interconversion of the isomerides. The  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated acids belong to this class, and the fact that considerable quantities of saturated hydroxy- or ethoxy-acids are often formed under the conditions of interconversion has led to the suggestion that such changes may proceed, not by preliminary separation of mobile hydrogen, but by preliminary addition of water or alcohol, followed by elimination of the addendum in a different direction. A detailed study of certain cases has shown that this alternative is not tenable.<sup>6</sup> Thus, under appropriate conditions the phenylbutenoic acids (VII and VIII)



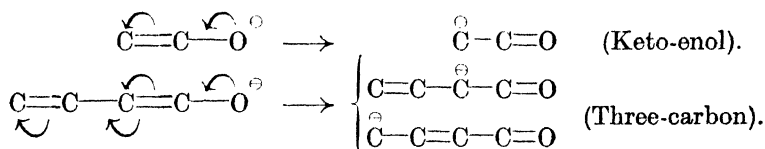
come into equilibrium rapidly, and continued treatment causes increased addition of water without noticeably affecting the proportion of the isomerides. Similarly, direct experiment has shown that the  $\beta$ -hydroxy-acid (IX) is formed too slowly, and when formed loses water too slowly, to be an intermediary in the interconversion of the isomerides (X) and (XI) :



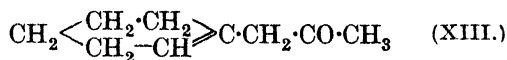
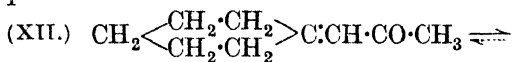
<sup>5</sup> The bracket {, an abbreviation of the large brackets { } of Werner's nomenclature, is taken as the symbol of an electrovalency; its position is intended to indicate the probable main location of the ionic charge.

<sup>6</sup> R. P. Linstead and L. T. D. Williams, *J.*, 1926, 2736; *A.*, 1926, 1245; Linstead, *J.*, 1927, 362; *A.*, 356; C. K. Ingold, C. W. Shoppee, and J. F. Thorpe, *J.*, 1926, 1477; *A.*, 1926, 939.

The influence of constitutional factors on tautomeric mobility and the correlation of the latter with other properties of the compound have been most fully investigated for the three-carbon system rendered mobile by the attachment of groups such as  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Alk}$ ,  $\text{CO}\cdot\text{Alk}$ , and  $\text{CN}$  to one of the terminal carbon atoms. A three-carbon system ( $\text{CH}\cdot\text{C}\cdot\text{C}\cdot\text{CO}\cdot\text{R} \rightleftharpoons \text{C}\cdot\text{C}\cdot\text{CH}\cdot\text{CO}\cdot\text{R}$ ) activated by a group of the form  $\cdot\text{CO}\cdot\text{R}$  bears a close resemblance to the keto-enol system ( $\text{CH}\cdot\text{CO}\cdot\text{R}$ ); in the former, however, there are three atoms instead of two amongst which the charge can be distributed in the electromeric anion, and therefore two points instead of one at which a cation (*e.g.*, hydrogen) can form a covalent link with carbon :<sup>7</sup>



The close correspondence between tautomeric mobility in general and those other properties such as the formation of stable sodium derivatives, ease of alkylation, etc., which also depend on the ionisability of the compound and the stability of its anion, was pointed out some years ago,<sup>8</sup> and this correspondence has been verified for the three-carbon system.<sup>9</sup> The necessary inference that those groups R (in  $\cdot\text{CO}\cdot\text{R}$ ) which best stabilise the ion of the enol in the keto-enol system should confer greatest mobility on the three-carbon system has also been confirmed. For example, whereas the acids (X) and (XI) can each be isolated and require hot alkali for their interconversion, the analogous ketones (XII) and (XIII) are so readily interconvertible that attempts to prepare them by the action of magnesium methyl iodide on the chlorides of the corresponding unsaturated acids lead to the same mixture, the physical properties of which approximate to those to be expected of the structure (XIII), although its chemical reactions (Michael's addition reaction and  $\alpha$ -alkylation) indicate that both forms are present.<sup>10</sup>



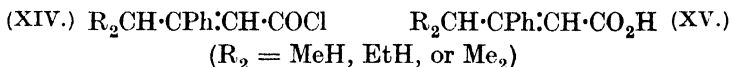
<sup>7</sup> C. K. Ingold, C. W. Shoppee, and J. F. Thorpe, *loc. cit.*

<sup>8</sup> C. K. Ingold and H. A. Figgott, *J.*, 1922, 121, 2381.

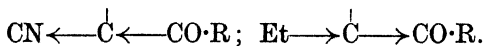
<sup>9</sup> G. A. R. Kon, *J.*, 1926, 1792; *A.*, 1926, 952.

<sup>10</sup> Dr. Kon informs the Reporter that the separate ketones (XII) and (XIII) have just been made, together with the two corresponding ethyl ketones, and the cyclopentane analogues of the latter.

It is consistent that, whereas the acids cannot be alkylated, the ketones, and even more readily the corresponding phenyl ketones ( $-\text{CO}\cdot\text{Ph}$ ),<sup>11</sup> can; and that generally amongst a series of unsaturated ketones the more mobile compounds can be  $\alpha$ -alkylated with greater facility than the more static, even although the latter may already be in the  $\beta\gamma$ -unsaturated form.<sup>9</sup> A similar contrast is found in the systems the  $\alpha\beta$ -modifications of which have the formulæ (XIV) and (XV).<sup>12</sup>



Here, whereas the acids undergo interconversion on heating with concentrated alkali, the acid chlorides pass into their isomerides at a similar temperature without the addition of a reagent. The esters of (X) and (XI) undergo interconversion rather easily,<sup>13</sup> although not so readily as the ketones (XII) and (XIII). On the whole, therefore, these results may be said to be consistent with the theoretical sequence  $\cdot\text{CO}\cdot\text{CH}_3 > \text{CO}\cdot\text{Cl} > \text{CO}\cdot\text{OR} > \text{CO}\cdot\text{O}^\ominus$  (indicated also by analogy with aromatic substitution) for the activating efficiency of groups terminating a three-carbon system.<sup>7</sup> The position of the cyano-group is difficult to determine on theoretical grounds, but experiment appears to show that it does not induce so high a degree of mobility as acetyl.<sup>14</sup> This may mean that the ionic group  $\text{C}\equiv\text{C}\cdot\text{N}^\ominus$  is less stable than the group  $\text{C}\equiv\text{C}\cdot\text{O}^\ominus$ , but it is important to observe that the above comparison of the cyano-group with acetyl applies only to the three-carbon system terminated by a *single* activating group; for it does not follow that the combination  $\begin{smallmatrix} \text{CN} \\ \diagdown \\ \text{CO}_2\text{R} \end{smallmatrix}$ , for example, will be found less effective in promoting mobility than  $\begin{smallmatrix} \text{CO}_2\text{R} \\ \diagdown \\ \text{CO}_2\text{R} \end{smallmatrix}$ , since in both an oxygen atom is available as the seat of the anionic charge, and the *indirect* effect of CN in stabilising the anion derived from the former group would be expected to be very great. It remains to be added that the introduction of an  $\alpha$ -alkyl group appears to diminish mobility,<sup>14</sup> and this behaviour is normal, since the alkyl group acts oppositely to the cyano-group in the preceding example; in other words, it tends to charge the neighbouring carbonyl oxygen atom negatively and thus diminishes its affinity for the anionic charge:



<sup>11</sup> M. D. Farrow and G. A. R. Kon, *J.*, 1926, 2128; *A.*, 1926, 1040.

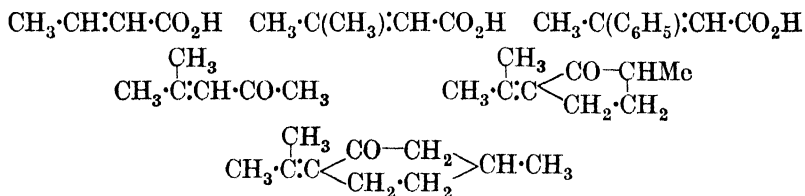
<sup>12</sup> J. D. A. Johnson and G. A. R. Kon, *ibid.*, p. 2748; *A.*, 1926, 1245.

<sup>13</sup> R. P. Linstead and C. J. May, *J.*, 1927, 2565; *A.*, 1167.

<sup>14</sup> G. A. R. Kon and B. T. Narayanan, *ibid.*, p. 1536; *A.*, 873. Compare S. F. Birch and G. A. R. Kon, *J.*, 1923, 123, 2440.

Interesting results have been obtained by Kon, Linstead and their collaborators in experiments on the effect of structure on the position of equilibrium—an investigation rendered possible by the development by Linstead of a method for the analysis of mixtures of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated isomerides.<sup>15</sup> In the first place, several results indicate that modifications of the activating group which play so large a part in the determination of the mobility of the system are of subsidiary importance in relation to the equilibrium. For example, for *cyclohexylidene*- and *cyclohexenyl*-acetic acids (really their anions, since the interconversion is carried out in alkaline solution) the equilibrium is (12%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (88%), whereas for the corresponding esters it is (10%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (90%); again, for the anions of the  $\beta$ -phenyl-*n*-butenoic acids the equilibrium is (25%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (75%), and for the corresponding acid chlorides it is (21%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (79%). The  $\beta$ -ethyl-*n*-pentenoic anions, (5%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (95%), show a rather larger difference from the corresponding methyl ketones (14%)  $\alpha\beta \rightleftharpoons \beta\gamma$  (86%), which is intelligible, since the activating groups  $\cdot\text{CO}\cdot\text{CH}_3$  and  $\cdot\text{CO}\cdot\text{O}^{13}$  are very dissimilar (compare the sequence).

On the other hand, the equilibrium is remarkably sensitive to substitutions in certain positions of the three-carbon system itself. When the  $\gamma$ -position is unsubstituted—for example, in crotonic acid,  $\beta\beta$ -dimethylacrylic acid,  $\beta$ -methylcinnamic acid, and *iso*-propylidene ketones such as mesityl oxide, camphorophorone<sup>16</sup> and pulegone<sup>17</sup>—the stable form is the  $\alpha\beta$ -unsaturated form, and it is



obvious from the examples that the substitution of methyl or even phenyl for hydrogen in the  $\beta$ -position makes no difference to this result; on the other hand, the introduction of a single methyl group into the  $\gamma$ -position causes the equilibrium to shift to the side of the  $\beta\gamma$ -unsaturated isomeride. This is exemplified in  $\beta$ -methyl- $\beta$ -ethyl-

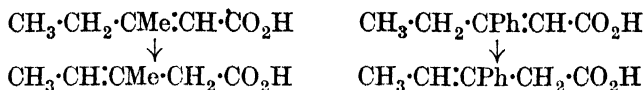
<sup>15</sup> This depends on their different rates of absorption of halogens (R. P. Linstead, *J.*, 1927, 353, 362; *A.*, 356; R. P. Linstead and C. J. May, *loc. cit.*).

<sup>16</sup> G. A. R. Kon and J. H. Nutland, *J.*, 1926, 3101; *A.*, 1926, 153.

<sup>17</sup> W. E. Hugh, G. A. R. Kon, and R. P. Linstead, *J.*, 1927, 2585; *A.*, 1195.



acrylic<sup>18</sup> and  $\beta$ -ethylcinnamic acids, the stable forms of which are the  $\beta\gamma$ -forms :<sup>12</sup>



The explanation which has been advanced<sup>7</sup> is that the  $\gamma$ -methyl group tends to charge the  $\gamma$ -carbon atom negatively, thus diminishing its affinity for the anionic charge; hence the eliminated proton recombines preferentially in the  $\alpha$ -position. When, however, in place of methyl, higher alkyl groups are introduced into the  $\gamma$  position, the effect on the equilibrium, instead of getting larger (as it should according to this explanation), gradually becomes less until in  $\beta\beta$ -diisobutylacrylic acid the proportion of the  $\alpha\beta$ - and  $\beta\gamma$ -isomerides present at equilibrium is about 1 : 1. The results for a series of acrylic acids,  $\text{RR}'\text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , are as follows :<sup>19</sup>

Open-chain acids.

Groups $\text{RR}'$ .....	$\text{Me}_2$	$\text{Et}_2$	$\text{Pr}^\alpha_2$	$\text{Bu}^\beta_2$
$\gamma$ -Substituent .....	- H	$-\text{CH}_3$	$-\text{CH}_2 \cdot \text{CH}_3$	$-\text{CH} \begin{array}{l} \nearrow \text{CH}_3 \\ \searrow \text{CH}_3 \end{array}$
Proportion of $\alpha\beta$ -form .....	100%	5%	33%	49%

Cyclic acids.

Ring $\text{RR}'\text{C}$ : .....	—	$(\text{CH}_2)_4 > \text{C}$	$(\text{CH}_2)_5 > \text{C}$	$(\text{CH}_2)_6 > \text{C}$
Proportion of $\alpha\beta$ -form .....	—	15%	12%	25%

The  $\beta$ -alkylcinnamic acids,  $\text{RR}'\text{CH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ , show a similar variation :

$\gamma$ -Substituents ( $\text{RR}'$ ) .....	$\text{H}_2$	$\text{CH}_3, \text{H}$	$\text{C}_2\text{H}_5, \text{H}$	$(\text{CH}_3)_2$
Proportion of $\alpha\beta$ -form .....	100%	25%	52%	54%

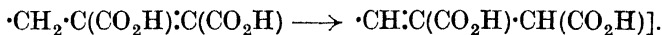
Clearly some new factor has entered here, and it is to be noted that those compounds which show the effect most strongly have a bulky group in the  $\beta$ -position as well as in the  $\gamma$ -position. The suggestion is<sup>19</sup> that a spatial effect is now under observation, and that it is connected with the known influence of *gem*-dialkyl groups in stabilising strained rings and ethylenic linkings. Thus in the first series the effect becomes maximal in the compound in which a *gem*-diisobutyl group stabilises the  $\alpha\beta$ -double bond in  $\text{Bu}^\beta_2\text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ ; and in the third series an almost equal action is exerted by the phenylpropyl group in  $\text{PhPr}^\alpha\text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H}$  and by the phenylisopropyl group in  $\text{PhPr}^\beta\text{C} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ . The results quoted give considerable support to this hypothesis, although the figures for the alicyclic compounds are admittedly difficult to explain. Nevertheless even these figures are not demonstrably inconsistent

<sup>18</sup> G. A. R. Kon and R. P. Linstead, *J.*, 1925, 127, 616; *A.*, 1925, i, 506.

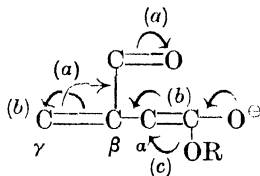
<sup>19</sup> G. A. R. Kon and C. J. May, *J.*, 1927, 1549; *A.*, 853.

with the theory; for it is evident that the conflict of polar and steric factors must produce a minimum somewhere in each series of homologues. In the first and the third series this minimum occurs at the second member; but in the *cycloalkylidene* acids the distinction between the  $\beta$ -group and the  $\gamma$ -group is indefinite, and this might conceivably cause the minimum to appear at *cyclohexylidene*. G. A. R. Kon and E. A. Speight<sup>20</sup> postulate a special attraction of the *cyclohexane* ring for the double linking.

The effect of an  $\alpha$ -alkyl group has as yet only been qualitatively investigated, and as the details are likely to be complex owing to the proximity of the activating group, it seems desirable to postpone discussion until further experiments have been performed. The effect of an additional group of the "activating" type (carboxyl, carbethoxyl, cyano) in the  $\alpha$ - or the  $\gamma$ -position is to increase mobility; in the former case, owing to increased possibilities of conjugation, it tends further to unbalance the system in the direction of the  $\alpha\beta$ -form, in the latter it tends to produce symmetry and thus to balance the equilibrium.<sup>20</sup> The effect of a carboxyl or carbethoxyl group in the  $\beta$ -position is, as is well known, to favour the  $\beta\gamma$ -form [*e.g.*, in the tetrahydrophthalic acids,



This has been discussed by Ingold, Shoppee, and Thorpe,<sup>7</sup> who point out that the affinity of the  $\beta$ -group for electrons (process *a*) will oppose the communication of the anionic charge to the  $\gamma$ -position (process *b*), and so favour combination with the proton in the  $\alpha$ -position (process *c*):



The study of the effect of constitutional influences on mobility and equilibrium in ring-chain tautomeric systems is in a less advanced state, but it may be taken that the limit towards which the phenomena tend is known. For example, constitutional effects in the keto-cyclol system show certain marked differences from those in the keto-enol system, and these differences must increase as the chain A, between the reacting groups, in



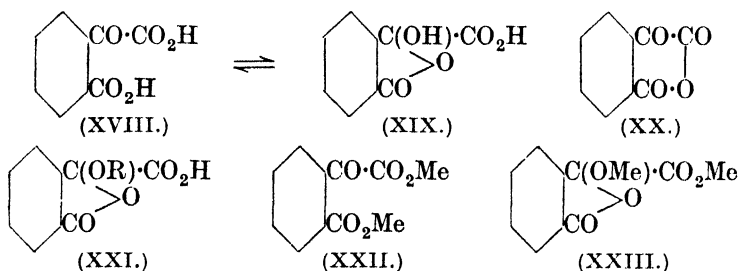
<sup>20</sup> *J.*, 1926, 2727; *A.*, 1926, 1246. See also G. A. R. Kon and J. H. Nutland, *ibid.*, p. 3101; *A.*, 1927, 163.

becomes longer until the conditions of the intermolecular (that is the aldol) reaction are approached. Similarly, the conditions controlling three-carbon ring-chain tautomerism will approximate to those governing the Michael reaction, which is a developed case of the aldol reaction, just as the system  $\text{CH}\cdot\text{C}\cdot\text{C}\cdot\text{C}\cdot\text{O}$  is a developed case of the system  $\text{CH}\cdot\text{C}\cdot\text{O}$  (above). The principal conditions governing these limiting cases, the reversible addition reactions, have recently been summarised.<sup>21</sup> In addition, it has to be remembered that spatial factors must always play a peculiarly important part in tautomerism involving ring closure, and examples illustrating this continue to accumulate; for instance, whereas  $\alpha\delta$ -diacetylbutane (XVI) is an ordinary  $\varepsilon$ -diketone, the  $\beta\beta\gamma\gamma$ -tetramethyl derivative passes into the cyclol (XVII) at the moment of formation, and all its reactions are those of this form : <sup>22</sup>



The two cases apparently represent extremes, the effect of the two *gem*-dimethyl groups in bringing the reacting residues into proximity being sufficiently great to produce a complete alteration of type.

Phthalonic acid is a better balanced example of ring-chain tautomerism of the keto-lactol type (XVIII, XIX) : it exhibits strong carbonyl reactivity, yields an ordinary anhydride (XX), and also displays the properties of a hydroxy-lactone in giving derivatives of the type (XXI). On esterification it yields two neutral dimethyl esters (XXII and XXIII), of which only the former gives a semicarbazone : <sup>23</sup>



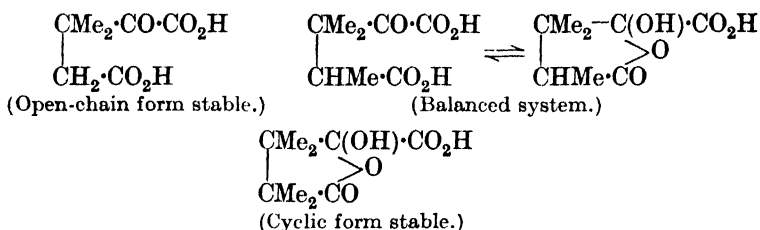
The analogy with Balbiano's acid ( $\gamma$ -keto- $\alpha\beta$ -trimethylglutaric acid) is obvious, and in connexion with the influence of *gem*-dimethyl groups in altering the balance of a ring-chain system the

<sup>21</sup> K. E. Cooper, C. K. Ingold, and E. H. Ingold, *J.*, 1926, 1868; *A.*, 1926, 938.

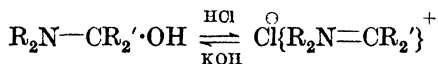
<sup>22</sup> I. Vogel, *J.*, 1927, 594; *A.*, 449.

<sup>23</sup> A. Cornillot, *Ann. Chim.*, 1927, [x], 7, 275; 8, 120; *A.*, 1069.

following comparison of Balbiano's acid with the lower and higher homologues is instructive : <sup>24</sup>



(2) *Mobile Anion Tautomerism (Anionotropy)*. *Special Case : Pseudo-basicity*.—The conditions obtaining here are in many respects the converse of those relating to the preceding section : the mobile group (*e.g.*, OH or Cl) becomes detached as an anion, leaving an electromeric cation in which the positive charge tends to distribution. The activating groups are therefore those which can provide a suitable seat for the positive charge, and groups containing tervalent nitrogen are, in general, the most efficient owing to the stability and strong tendency to formation of the ammonium condition (*e.g.*,  $\text{R}_2\text{N} \xrightarrow{\oplus} \text{CR}_2' \longrightarrow \text{R}_2\text{N}^{\oplus} = \text{CR}_2'$ ;  $\text{R} \cdot \text{N} \xrightarrow{\oplus} \text{N} \longrightarrow \text{R} \cdot \text{N}^{\oplus} \equiv \text{N}$ ). Again, in the same way that in mobile cation tautomerism the hydrogen ion forms a more or less stable covalent link with (negative) carbon, whereas the sodium ion tends to remain in the electrovalent state (thus giving rise to the phenomena of pseudo-acidity), so, in the case now under consideration, the hydroxide ion tends to co-ordinate with (positive) carbon, whereas very stable anions like chloride and perchlorate tend to retain their ionic condition in an electrovalent link : thus arises the phenomenon of pseudo-basicity,



as exemplified by acridinium salts, hydrastinine and its analogues, and the dyes of the magenta group (in which group the cation is quinonoid and coloured).

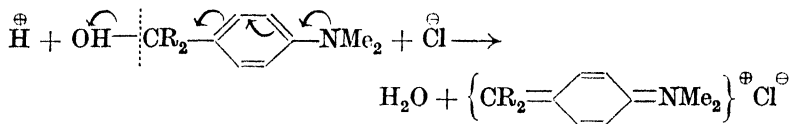
The above is a generalised form of W. Madelung's theory <sup>25</sup> of the constitution of the last-mentioned group of compounds, <sup>26</sup> and some interesting applications have been made. For example,

<sup>24</sup> E. Rothstein and C. W. Shoppee, *J.*, 1927, 531; *A.*, 447.

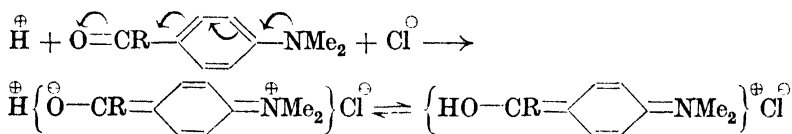
<sup>25</sup> *J. pr. Chem.*, 1925, [ii], 111, 100; *A.*, 1925, i, 1459.

<sup>26</sup> Separate discussion is required regarding the effect, in stabilising the quinonoid cation, of the additional aryl residues attached to the methane carbon atom in di- and tri-arylmethane derivatives.

analogy with the formation of ordinary di- and tri-phenylmethane dye-salts from their pseudo-bases



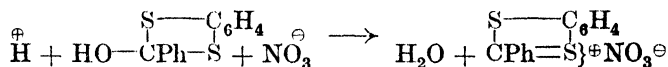
suggests that the carbonyl group in *op*-amino-ketones may possess the power of functioning as a pseudo-basic centre without fission of the molecule :



This has been verified by W. Madelung and F. Völker<sup>27</sup> in the case of Michler's ketone (*pp'*-tetramethyldiaminobenzophenone), the monoperchlorate of which is a dye-salt having an absorption curve similar to that of auramine. There is evidence that a corresponding change can proceed to some extent even when an ethenoid group replaces the carbonyl group in the above ketone, for the *pp'*-tetramethyldiamino-*as*-diphenylethylenes (XXIV, XXV and XXVI) yield coloured salts in alcoholic perchloric acid, which are, however, rather unstable, since they are destroyed by addition of water with precipitation of the original ethylene derivative.<sup>28</sup>



Although less stable than the ammonium condition, the thionium condition possesses considerable stability and tendency to formation, and it is therefore of great interest that W. R. H. Hurtley and S. Smiles have succeeded in preparing a series of sulphur pseudo-bases from *o*-dithiolbenzene.<sup>29</sup> This substance on condensation with benzaldehyde yields a phenylbenzodithiole which on oxidation gives a compound with the properties of a typical pseudo-base :



<sup>27</sup> *J. pr. Chem.*, 1926, [ii], 114, 1; *A.*, 1927, 54.

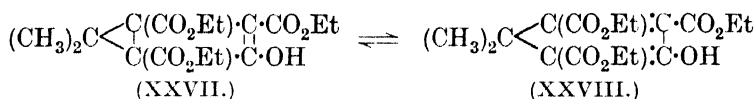
<sup>28</sup> *Idem, ibid.*, 1927, [ii], 115, 24; *A.*, 146.

<sup>29</sup> *J.*, 1926, 1821; 1927, 534; *A.*, 1926, 948; 1927, 466.

The salts appear to be definitely more stable than those of the few known oxygen pseudo-bases such as xanthhydryl.

That mobile anion tautomerism may occur in the absence of an -onium group (excepting that carbon may temporarily assume the "carbonium" condition with a sextet of electrons), provided that the mobile cation has sufficient stability, is clear from many facts, including the recent observations of C. Prévost on the isomerisation of  $\alpha$ - and  $\gamma$ -substituted allyl bromides.<sup>30</sup>

(3) *Valency Tautomerism. Special Case: Intra-annular Tautomerism.*—In valency tautomerism the positive and the negative charges simultaneously produced by the movement of a double linking are neutralised by the concomitant movement of a second double linking, so that ions do not separate in the process. The phenomenon is exhibited *par excellence* in ring-compounds such as the derivative (XXVII, XXVIII) of dicyclopentene (cyclopentadiene) first prepared by W. H. Perkin and J. F. Thorpe :<sup>31</sup>

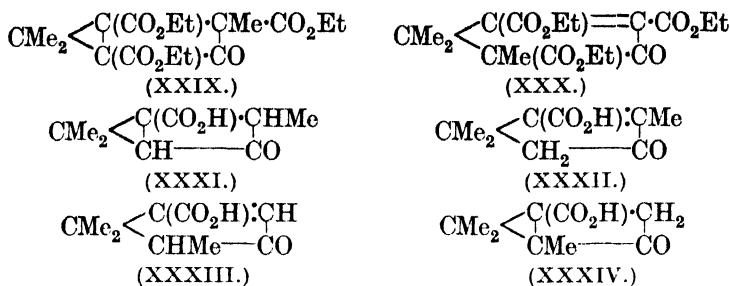


An important paper on this subject has recently been published by J. Toivonen,<sup>32</sup> and, as the result, an interesting position has now been reached in the study of this compound and the class it represents. When the above hydroxy-ester is methylated through its sodio-derivative, a liquid *C*-methylation product is obtained to which formula (XXIX) or (XXX) may be assigned. This, on hydrolysis, yields a somewhat ill-defined monobasic acid which may possess any of the constitutions (XXXI—XXXIV). The formulæ (XXIX) and (XXX) obviously represent static derivatives in which the intra-annular tautomeric system is blocked by substitution, and it is therefore of interest to determine the direction in which blocking has been effected.

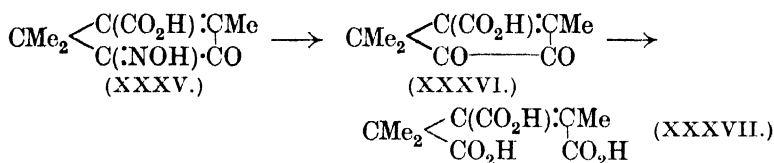
<sup>30</sup> *Compt. rend.*, 1927, **184**, 458, 1460; **A.**, 337, 748. See also a paper by E. H. Farmer, B. D. Laroia, T. M. Switz, and J. F. Thorpe (*J.*, 1927, 2937), which appeared after the above was written and deserves fuller reference than this mere citation.

<sup>31</sup> *J.*, 1901, **79**, 729. As to the structure, see J. Toivonen, *Annalen*, 1919, **419**, 176; *A.*, 1920, i, 49; E. H. Farmer and C. K. Ingold, *J.*, 1920, **117**, 1362; E. H. Farmer, C. K. Ingold, and J. F. Thorpe, *J.*, 1922, **121**, 128; J. Toivonen, *Acta Sci. Fennicae, Comm. Phys.-Math.*, I, 1922, **26**, 1; *A.*, 1923, i, 1017; R. C. Grimwood, C. K. Ingold, and J. F. Thorpe, *J.*, 1923, **123**, 3303.

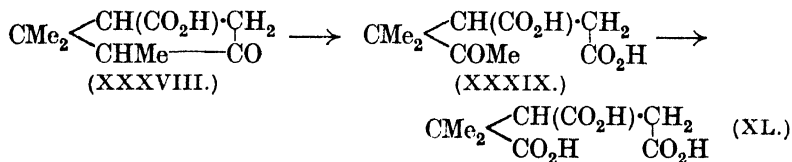
<sup>32</sup> *Ann. Acad. Sci. Fennicae*, 1927, **19**, No. 20.



Grimwood, Ingold, and Thorpe<sup>33</sup> contributed the following data to this problem: when the monobasic acid is treated with amyl nitrite and hydrochloric acid, 30% of an oximino-derivative is formed; this must possess the constitution (XXXV) (derived from XXXII), because on hydrolysis it gives an  $\alpha$ -diketone (XXXVI), which with hydrogen peroxide yields trimethylaconitic acid (XXXVII). Excepting that chlorination products were recognised, the fate of the remainder of the material was not traced:

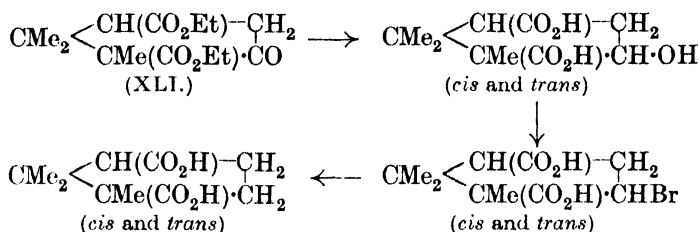


Toivonen<sup>32</sup> proceeded in a different way. He reduced the methylation product (XXIX, XXX), hydrolysed the reduced substances, and from the crude acid product (68%) isolated by crystallisation a pure acid. This acid, which was also obtained by hydrolysis of the methylation product and subsequent reduction, was proved to have formula (XXXVIII), because on oxidation it yielded a methyl ketone (XXXIX) together with dimethyltricarballic acid (XL):

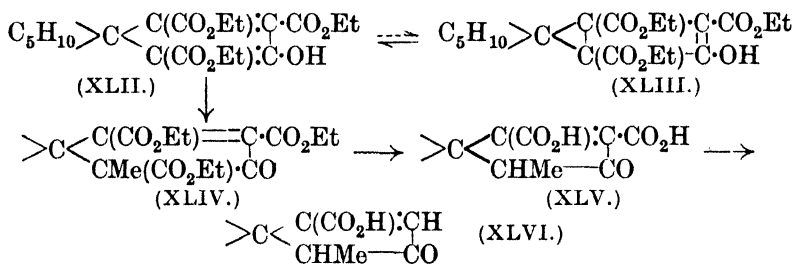


The evidence is therefore very strong that blocking occurs in both directions in the methylation of the tautomeric ester-enol (XXVII, XXVIII), and a provisional estimate by Toivonen based on oxidation experiments is that the methylation product contains 28% of (XXIX) and 72% of (XXX).

A by-product of the work was the completion of a new synthesis of camphoric acid. The ester (XLI), an intermediate in the hydrolysis of the reduced methylation product, on further hydrolysis and reduction in the manner indicated yields racemic camphoric acid :



It has been shown<sup>34</sup> that in the series of analogues derived from the *spirocyclohexane* compound (XLII, XLIII) the bridged phase is less pronounced than in the *gem*-dimethyl series. It is therefore consistent to find that no oximino-derivative (or, at most, a trace) analogous to (XXXV) can be obtained by the action of amyl nitrite and hydrochloric acid on the monobasic acid (XLVI), which is obtained by complete hydrolysis of the methylation product (XLIV); and that the intermediate dibasic acid (XLV) also undergoes reactions showing that it has the constitution indicated :<sup>35</sup>



### Natural Products. I. The Terpene Group.

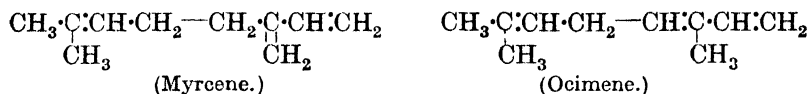
(1) *Monoterpene Compounds*.—In view of the probability that the monoterpenes or their more immediate derivatives constitute an intermediate stage in the phytochemical synthesis of the higher terpenes, it is important that knowledge of the structures of the simpler natural terpenes should be as accurate and complete as possible. At the present time, two natural open-chain monoterpenes are recognised, namely, myrcene from Bay oil and ocimene from oil of *Ocimum basilicum*. They both contain the geraniol

<sup>34</sup> C. K. Ingold, E. A. Seeley, and J. F. Thorpe, *J.*, 1923, **123**, 853.

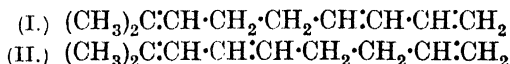
<sup>35</sup> C. K. Ingold and E. A. Seeley, *J.*, 1927, 1684; *A.*, 877.



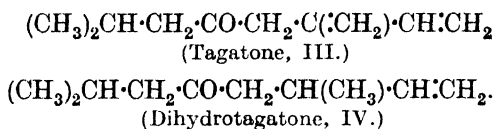
chain and differ only in the disposition of the conjugated double linkings : <sup>36</sup>



N. Hirano reports <sup>37</sup> the isolation of a third, termed "cryptotænene," from *Cryptotænia Japonica*, Hassk.; and, since its triozone on decomposition yields formic acid, acetone, succinic acid and a carbonyl compound, it is assigned either of the formulæ (I) and (II) :



This conclusion excites interest, for neither of the structures is divisible into isoprene units; should it be confirmed, it would revolutionise present ideas regarding the methods by which terpene structures are built up. It may, however, be suggested that the products obtained by ozonolysis do not seem to be inconsistent with the formula of myrcene (which is known to give succinic acid and acetone on oxidation); and that, having regard to the fact that the cryptotænene examined could not have been pure, since its optical activity was perceptible ( $[\alpha]_D^{20} + 2.66^\circ$ ), the agreement between its refractive index ( $n_D^{20}$  1.4748) and that of myrcene ( $n_D^{19}$  1.4700) appears sufficiently close to warrant the assumption of identity. The significance of the myrcene structure in the chemistry of the diterpenes is referred to below. Two ketones of the myrcene series, tagatone (III) and dihydrotagatone (IV), occur, along with ocimene, in the volatile oil of the *Tagates glandulifera* : <sup>38</sup>



Since the date of Meerwein's demonstration of the mechanism of the borneol-camphene change, and that of the synthesis of camphenilone by Komppa and Lipp, Aschan's alternative (VI) to the Wagner formula for camphene (V) has been obliterated from serious consideration. Nevertheless, the recent synthesis <sup>39</sup> of the Aschan structure forms an interesting pendant to a pre-war problem. The new hydrocarbon is called "endocamphene." It is a liquid

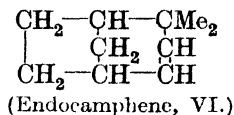
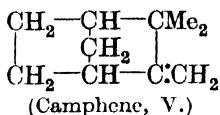
<sup>36</sup> C. J. Enklaar, *Rec. trav. chim.*, 1907, **26**, 157; 1908, **27**, 422; *A.*, 1908, i, 934.

<sup>37</sup> *J. Soc. Chem. Ind. Japan*, 1926, **29**, 48; *Bull. Chem. Soc. Japan*, 1926, **1**, 74; *A.*, 1926, 408.

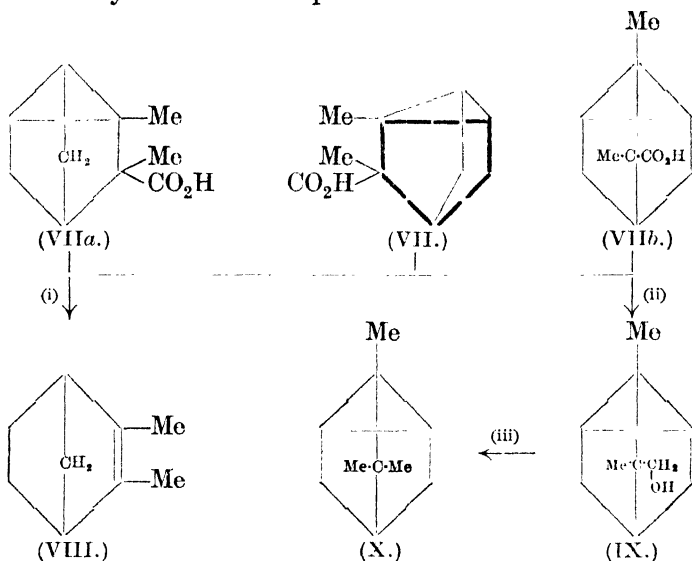
<sup>38</sup> T. G. H. Jones and F. B. Smith, *J.*, 1925, **127**, 2530; *A.*, 1926, 72.

<sup>39</sup> P. Lipp, A. Götzén, and F. Reinartz, *Annalen*, 1927, **453**, 1; *A.*, 568.

substance, and, needless to say, it is not camphene; nor has it been identified with any other naturally occurring terpene.



Teresantalic acid, which is present in sandal-wood oil and is one of the few known naturally occurring acids of the simple terpene series, has been proved<sup>40</sup> to possess the structure represented by formula (VII), of which (VIIa) and (VIIb) are plane projections;<sup>41</sup> and its relationship with santene (VIII) and tricyclene (X) (which is closely related to both bornylene and camphene) well illustrates the mutability of the monoterpene framework:

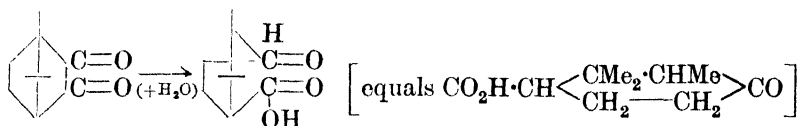


Reaction (i) takes place when the calcium salt of teresantalic acid is heated; reduction (ii) of the ester yields teresantalol (IX); process (iii) represents the oxidation of this to the corresponding aldehyde and the reduction of the semicarbazone of the latter with sodium ethoxide (Wolff's method). Since the constitutions of santene and tricyclene are known, these reactions determine that of teresantalic acid.

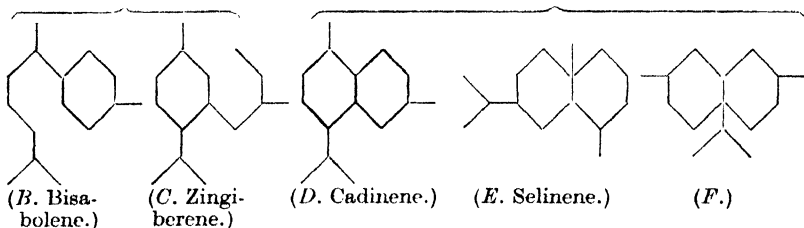
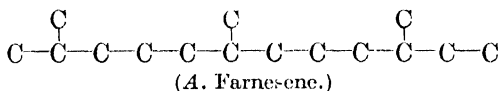
<sup>40</sup> L. Ruzicka and F. Liebe, *Helv. Chim. Acta*, 1926, 9, 140; *A.*, 1926, 400.

<sup>41</sup> Some confusion has arisen in the literature owing to failure to recognise that formulæ of the type of (VIIa) and (VIIb) are the same.

A change related to the Wagner re-arrangement, but presenting certain peculiarities, is undergone by camphorquinone in the presence of sulphuric acid. The product is a ketonic acid in the formation of which one of the *cyclopentane* rings has been broken and the other enlarged :<sup>42</sup>



(2) *Sesquiterpene Compounds*.—Since this subject was last reported, much valuable work has been done in filling in the details of the picture then outlined. Farnesene, which may be regarded as the parent of the  $\text{C}_{15}$ -group, just as myrcene may be considered to be the parent of the  $\text{C}_{10}$ -group, contains the carbon chain (A), and this, by cyclisation in accordance with the laws which appear to govern the development of terpene structures, can yield two monocyclic types, (B) and (C), and three dicyclic types, (D), (E), and (F). Natural terpenes of all these types except the last are now known, and the structure of one example of each group has been more or less completely elucidated. These examples are mentioned by name below the formulæ :

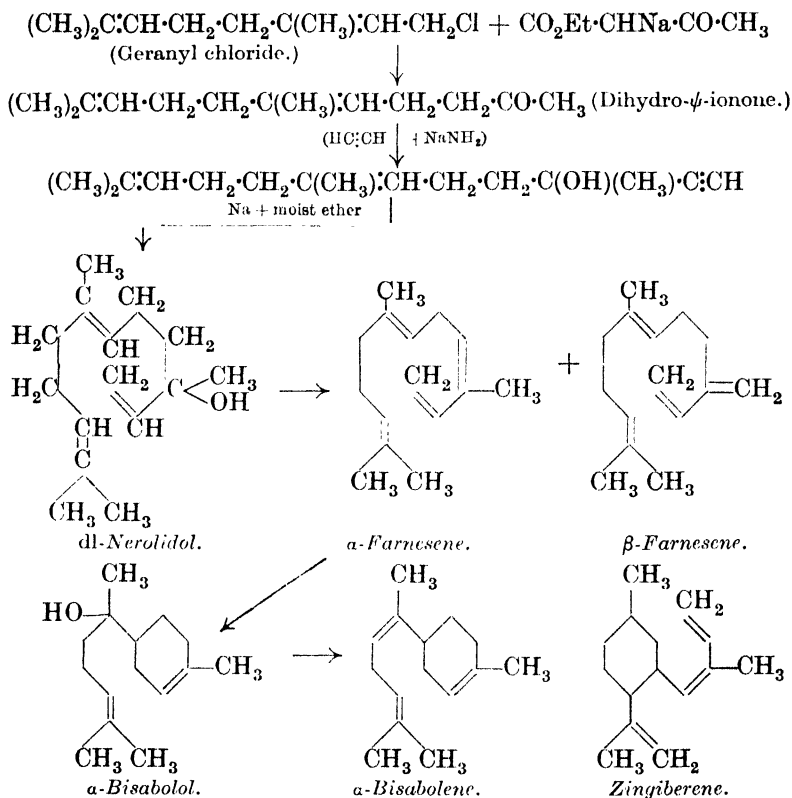


When farnesene is treated with acetic acid containing a little sulphuric acid it is converted into the acetate of  $\alpha$ -bisabolol (analogue of  $\alpha$ -terpineol); this alcohol on treatment with hydrogen chloride yields a trihydrochloride, m. p.  $79^\circ$ , identical with that of natural bisabolene from oil of *Opopanax*.<sup>43</sup> Since farnesene has been

<sup>42</sup> C. S. Gibson and J. L. Simonsen, *J.*, 1925, **127**, 1294; *A.*, 1925, i, 919; M. B. Bhagvat and J. L. Simonsen, *J.*, 1927, 77; *A.*, 250; M. Bredt-Savelsberg, K. Zaunbrecher, and L. Knieke, *Ber.*, 1927, **60**, [B], 1801; *A.*, 1068.

<sup>43</sup> L. Ruzicka and E. Capato, *Helv. Chim. Acta*, 1925, **8**, 259; *A.*, 1925, i, 943.

synthesised<sup>44</sup> from geranyl chloride by way of dihydro- $\psi$ -ionone (analogue of methylheptenone) and nerolidol (analogue of linalool), these reactions constitute a synthesis of bisabolene :

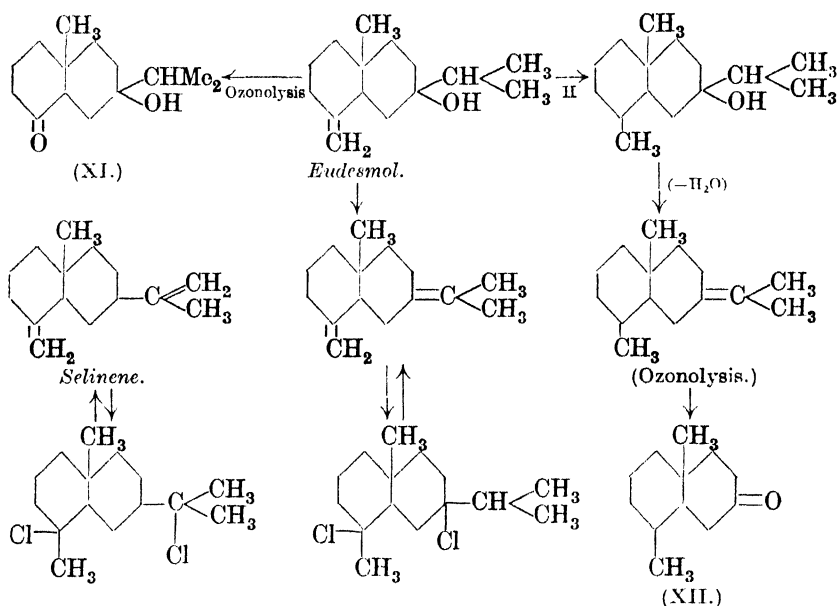


Zingiberene probably has the structure shown; the constitutions of cadinene and selinene were dealt with in a previous report.<sup>45</sup> Lately the constitution of eudesmol, the important sesquiterpene alcohol from eucalyptus, has been definitely ascertained. Sulphur-dehydrogenation had shown that the carbon framework was the same as that of selinene. The position of the double link has now been revealed by the observation that ozonolysis removes one carbon atom and yields a methylisopropyldecalolone (XI). The tertiary hydroxyl group cannot form part of a side chain  $-\text{C}(\text{OH})\text{Me}_2$ , because eudesmene dihydrochloride and selinene dihydrochloride are not identical, and therefore it is located in the position shown

<sup>44</sup> L. Ruzicka, *Helv. Chim. Acta*, 1923, **6**, 492; *A.*, 1923, **i**, 691.

<sup>45</sup> *Ann. Reports*, 1924, **21**, 99.

by the fact that dihydroeudesmene on ozonolysis loses three carbon atoms, giving a dimethyldecalone<sup>46</sup> (XII) :



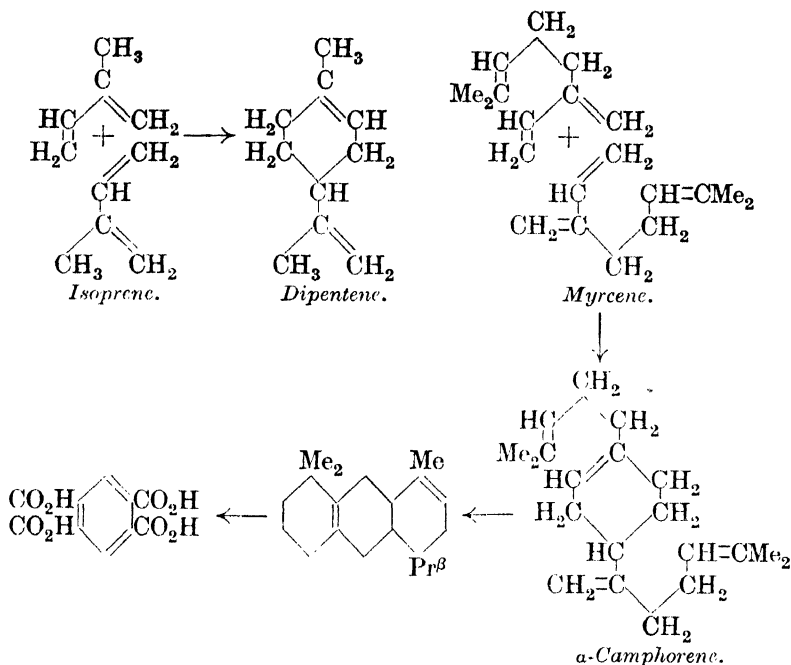
Recent work enables approximate formulæ to be developed for the tricyclic terpenes copæne and santalene, the former of which appears to possess a bridge of the sabinene type; these structures are, however, not yet definitely confirmed. An attack on the structure of elemol and on the higher terpene products from Manila copal has also been opened.<sup>47</sup>

(3) *Diterpene Compounds*.—The diterpene framework may be regarded as primarily arising, not only by polymerisation of isoprene units, but also (and more probably) by dimerisation of monoterpene units. Thus, just as isoprene dimerises to dipentene, so myrcene might dimerise to a monocyclic diterpene of the structure indicated. There can be little doubt that  $\alpha$ -camphorene (from camphor oil) has this constitution, for dehydrogenation followed by oxidation yields terephthalic acid, and cyclisation with formic acid produces a hydroanthracene derivative, as is proved by its degradation to pyromellitic acid:<sup>48</sup>

<sup>46</sup> L. Ruzicka and E. Capato, *Annalen*, 1927, **453**, 62; **A.**, 570.

<sup>47</sup> L. Ruzicka and M. Pfeiffer, *Helv. Chim. Acta*, 1926, **9**, 841; **A.**, 1926, 1148; L. Ruzicka, R. Steiger, and H. Schinz, *ibid.*, p. 962; **A.**, 1927, 60.

<sup>48</sup> L. Ruzicka and M. Stoll, *ibid.*, 1924, **7**, 271; **A.**, 1924, i, 532.

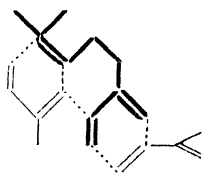
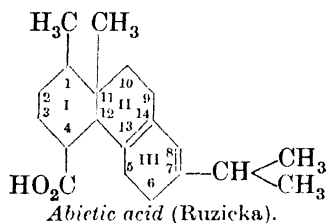


The known diterpene acids, which are all obtained from natural resins, contain the hydrophenanthrene skeleton. They fall into two series, the first comprising *d*- and *l*-abietic acids, which are true optical enantiomorphs, pinabietic acid, which may be identical with one of them, and *l*-pimaric acid, which is closely related to the abietic acids in some way not yet understood; these give retene (1-methyl-7-*isopropyl*phenanthrene) on dehydrogenation with sulphur, one carbon atom (methyl group) being lost in addition to the carboxyl group during the process. The second series is represented by *d*-pimaric acid, which gives a dimethylphenanthrene on dehydrogenation; here three carbon atoms (*isopropyl* group) together with the carboxyl group are lost in the reaction.

More detailed knowledge of the structure of abietic acid has been obtained mainly by a study of its products of oxidation and reduction.<sup>49</sup> Mild oxidation yields a dihydroxy- and then a tetrahydroxy-derivative, showing the presence of two double bonds, one of which is more reactive than the other. Similarly, on reduc-

<sup>49</sup> A. I. Virtanen, *Annalen*, 1921, **424**, 150; *A.*, 1921, i, 669; L. Ruzicka, H. Schinz, and J. Meyer, *Helv. Chim. Acta*, 1923, **6**, 1077, 1097; *A.*, 1924, i, 171, 172; L. Ruzicka, J. Meyer, and M. Pfeiffer, *ibid.*, 1925, **8**, 632, 637; *A.*, 1925, i, 1419; M. G. Rau and J. L. Simonsen, *J. Indian Inst. Sci.*, 1926, **9**, 111; *A.*, 1926, 1246; O. Aschan, P. Levy, and H. Brunotte, *Ber.*, 1927, **60**, [B], 1923; *A.*, 1067.

tion two atoms of hydrogen are added, and then, less readily, a further two. Oxidation by nitric acid yields *isophthalic acid* and *trimellitic acid* (benzene-1:2:4-tricarboxylic acid). Oxidation under conditions which especially favour dehydrogenation yields *trimellitic acid* and *mellophanic acid* (the 1:2:3:4-acid), and oxidation of dihydroabietene (derived from abietic acid by the elimination of the carboxyl group and the addition of two atoms of hydrogen to a double bond) yields *mellophanic acid* unaccompanied by the tribasic acid. These facts can be explained if it is assumed that the rings II and III attain the aromatic condition, and thus survive, in the oxidation of abietic acid, whereas, if the double bond at 7—8 is first reduced, only the central ring becomes aromatic:



Myrcene chain in 4 : 1-formula.

The loss of a methyl group during dehydrogenation to retene is taken to show that this group occupies one of the positions 11, 12, 13, and 14. Methylabietin (derived from abietic acid by a process of degradation which replaces  $\text{--CO}_2\text{H}$  by  $\text{--CH}_3$  and removes two atoms of hydrogen from the adjacent ring) on dehydrogenation yields methylretene; it follows that the carboxyl group in abietic acid does not occupy any of the above four positions; and furthermore, since methylretene on oxidation with chromic acid yields a phenanthraquinone, the carboxyl group is excluded from positions 9 and 10, and hence from the whole of ring II. Also, since methylabietin is oxidised to trimellitic acid, it is improbable that the carboxyl group in abietic acid is in ring III (since this ring would be aromatic in methylabietin), and its location is therefore limited to positions 2, 3, and 4 in ring I. The principle of division into isoprene units reduces the number of possibilities; the following combinations of positions for the carboxyl and labile methyl groups have been considered, namely,  $\text{CO}_2\text{H}:\text{Me} = 2:12, 2:11, 3:11, 4:11$ , and the 4:11-formula (above) is selected provisionally for purposes of illustration. There are, however, two other formulæ consistent with the isoprene rule, namely, 4:1 and 3:1, if count is taken of the possibility that both methyl groups might occupy the same nuclear position (position-1), just as in cyclised  $\alpha$ -camphorene. There appears to be no reason at present to exclude this

interpretation, and the additional formulæ may be worth mentioning, since they contain, in addition to two isoprene units, the myrcene chain with properly distributed unsaturation. The position of the oxidised carbon atom presents no great difficulty, since the corresponding isoprene unit may originally have formed part of a tagatone residue. The recognition of *isobutyric* and *succinic* acids amongst the oxidation products of abietic acid indicates that the double linkings are in the positions assigned to them, and the isolation of an unoriented dimethylcyclohexanetricarboxylic acid and its higher homologue, dicarboxydimethylcyclohexaneacetic acid, in the formation of which ring I has apparently survived, constitutes further evidence in the same direction. The orientation of either of these acids would settle the structure of abietic acid definitely.

The problem of the structure of *d*-pimaric acid is less advanced, and although a formula has been tentatively proposed, numerous alternatives are equally possible. It is established<sup>50</sup> that the acid contains a hydrophenanthrene skeleton which is related to the missing sesquiterpene structure (*F*, p. 122) in the sense that the *isopropyl* chain occupies one of the positions common to two rings. In addition, there are two methyl groups, a carboxyl group, and two double bonds; but all that can be said with reasonable assurance about these is that the groups are exclusively in the lateral rings and that the double bonds are in conjugated positions in that lateral ring which does not bear the carboxyl group.

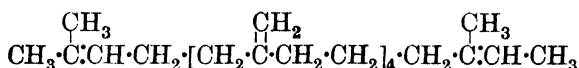
(4) *Triterpene Compounds*.—An attack upon the triterpene group has been opened by Heilbron and his collaborators with conspicuous success.<sup>51</sup> Squalene, which occurs in the livers of elasmobranch fish, is an open-chain dihydrotriterpene,  $C_{30}H_{50}$ , having six double linkings; the alleged isolation by previous workers of the homologues  $C_{29}H_{48}$  and  $C_{31}H_{52}$  has been controverted. On the other hand, squalene may be a mixture of isomerides, since it gives three distinct (isomeric) crystalline hexahydrochlorides. Hydrogenation proceeds in six fairly well-marked stages, yielding ultimately squalane (dodecahydrosqualene). On heating, squalene breaks down, giving compounds of the hemiterpene, monoterpene, sesquiterpene, and diterpene series. The hemiterpene product has been identified as the *isoamylene*  $CMe_2:CHMe$ ; the sesquiterpene is

<sup>50</sup> L. Ruzicka and F. Balas, *Helv. Chim. Acta*, 1924, **7**, 875; *A.*, 1924, **i**, 1311.

<sup>51</sup> I. M. Heilbron, E. D. Kamm, and W. M. Owens, *J.*, 1926, 1630; *A.*, 816; I. M. Heilbron, T. P. Hilditch, and E. D. Kamm, *ibid.*, p. 3131; *A.*, 1927, 130; J. Harvey, I. M. Heilbron, and E. D. Kamm, *ibid.*, p. 3136; *A.*, 1927, 130. Compare M. Tsujimoto, *Chem. Umschau*, 1927, **34**, 256; *A.*, 1051.



almost certainly a bisabolene. Cyclisation with formic acid closes four rings, two double links remaining. On dehydrogenation with sulphur, tetracyclosqualene yields a small amount of an oil resembling cymene, and a new naphthalene hydrocarbon (m. p. 33·5°) of the formula  $C_{13}H_{14}$ ; the same compound is produced when the sesquiterpene fraction obtained by destructively distilling tetracyclosqualene is similarly dehydrogenated. The isolation of bisabolene shows that at least one half of the squalene molecule must contain the farnesene chain, and accordingly the structure



is provisionally suggested. Apparently squalene is one of a family of triterpene products related to metabolic processes, for H. J. Channon and G. F. Marrian<sup>52</sup> have obtained from mammalian livers a squalene-like hydrocarbon, which, however, is not squalene.

### Natural Products. II. The Cholane Group.

The chemistry of the cholane series includes that of the bile acids, which is somewhat elaborate and does not appear to have been summarised previously in these Reports. Recent investigations have shown that these acids form part of an intimately related group of natural products, which includes also the two sterols, cholesterol and coprosterol.

The following are amongst the better-known bile acids :

Name.	Synonym.	Formula.	Source. <sup>53</sup>
Cholic acid.	Cholalic acid.	$C_{24}H_{40}O_5$	Man, ox, goat, sheep.
Deoxycholic acid.	Choleic acid.	$C_{24}H_{40}O_4$	Man, ox, goat, sheep.
Chenodeoxycholic acid.	Anthropodeoxycholic acid.	„	Man, goose, hen, ox.
Hyodeoxycholic acid.	Hyocholeic acid.	„	Pig.
Lithocholic acid.	—	$C_{24}H_{40}O_3$	Man, ox.

They occur in bile, to some extent in the free state, but for the most part as salts of their amides with glycine or taurine. Other acids have been isolated from the polar bear and walrus, and one other, namely, fellic acid, from man.

<sup>52</sup> *Biochem. J.*, 1926, **20**, 409; *A.*, 1926, 638.

<sup>53</sup> H. Wieland and G. Reverey, *Z. physiol. Chem.*, 1924, **140**, 186; *A.*, 1925, i, 181; A. Windaus, A. Böhne, and E. Schwarzkopf, *ibid.*, p. 177; *A.*, 1925, i, 405; M. Schenk, *ibid.*, 1925, **145**, 95; *A.*, 1925, i, 854; H. Wieland and R. Jacobi, *ibid.*, 1925, **148**, 232; *A.*, 1925, i, 1488; M. Schenk, *ibid.*, p. 218; *A.*, 1925, i, 1488; H. Wieland and P. Weyland, *ibid.*, 1920, **110**, 123; *A.*, 1921, i, 178; A. Windaus, *Z. angew. Chem.*, 1923, **36**, 309; *A.*, 1923, i, 922.

Cholic acid is a monobasic trihydroxy-acid, the three deoxycholic acids are monobasic dihydroxy-acids, and lithocholic acid is a monobasic monohydroxy-acid; they are all fully saturated and therefore contain four completely hydrogenated rings. On dehydration cholic acid loses  $3\text{H}_2\text{O}$ , giving cholatrienic acid, the three deoxycholic acids lose  $2\text{H}_2\text{O}$ , yielding the corresponding deoxycholadienic acids, and lithocholic acid loses  $\text{H}_2\text{O}$ , giving lithocholenic ("cholonic") acid; all these unsaturated acids on catalytic reduction give the same cholanolic acid,  $\text{C}_{24}\text{H}_{40}\text{O}_2$  <sup>54</sup> (hyodeoxycholadienic acid gives the stereoisomeric *allocholanolic* acid <sup>55</sup> in addition). Hence all the acids possess a common carbon framework.

It had long been surmised,<sup>56</sup> mainly on biological grounds, that this skeleton is intimately related to that of cholesterol ( $\text{C}_{27}\text{H}_{46}\text{O}$ , 4 rings, 1 hydroxyl, 1 double bond) and its spatially inverted dihydro-derivative coprosterol ( $\text{C}_{27}\text{H}_{48}\text{O}$ , 4 rings, 1 hydroxyl). The latter, together with dihydrocholesterol, is formed from cholesterol by the action of intestinal bacteria, and to some extent also by catalytic reduction at an elevated temperature.<sup>57</sup> Direct proof of a connexion was, however, first obtained by A. Windaus and K. Neukirchen in 1919.<sup>58</sup> It was known that cholesterol gives acetone on oxidation and that cholic and cholanolic acids do not, and examination of the formulæ of the saturated hydrocarbons cholestane (synonym  $\beta$ -cholestane) and  $\psi$ -cholestane (synonym coprostane), obtained from the saturated alcohols through the corresponding chlorides, shows that the oxidative fission of an *isopropyl* group from the end of a side chain,  $-\text{CH}_2\cdot\text{CH}(\text{CH}_3)_2 \longrightarrow -\text{CO}_2\text{H} + \text{CO}(\text{CH}_3)_2$ , should produce an acid having the composition of cholanolic acid. This degradation of the hydrocarbons was realised by oxidation with chromic acid; but it was coprostane which yielded the known cholanolic acid; cholestane yielded the previously unknown stereoisomeride, *allocholanolic* acid, the preparation of which from a bile acid has only recently been accomplished.<sup>59</sup>

<sup>54</sup> H. Wieland and F. J. Weil, *Z. physiol. Chem.*, 1912, **80**, 287; *A.*, 1912, i, 830; H. Wieland and H. Sorge, *ibid.*, 1916, **98**, 59; *A.*, 1917, i, 685; H. Wieland and P. Weyland, *ibid.*, 1920, **110**, 123; *A.*, 1921, i, 178; A. Windaus, A. Bohne, and E. Swarzkopf, *loc. cit.*; A. Windaus, *Annalen*, 1926, **447**, 223; *A.*, 1926, 732.

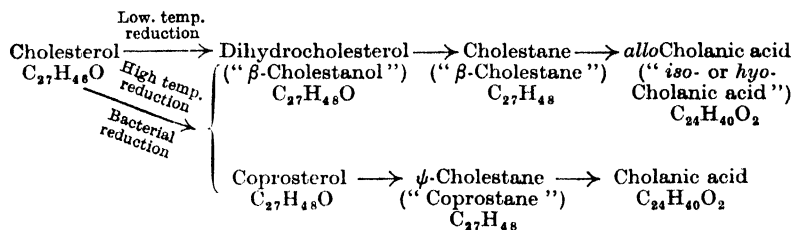
<sup>55</sup> Synonyms: "*isocholanolic* acid" and "*hyocholanolic* acid."

<sup>56</sup> I. Lifschütz, *Ber.*, 1914, **47**, 1459; *A.*, 1914, i, 657.

<sup>57</sup> *Ann. Reports*, 1917, **14**, 111.

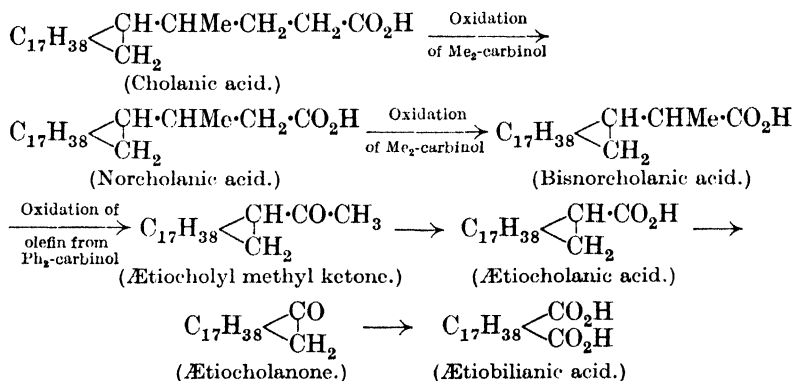
<sup>58</sup> *Ber.*, 1919, **52**, [B], 1915; *A.*, 1920, i, 41.

<sup>59</sup> A. Windaus, *Annalen*, 1926, **447**, 223; *A.*, 1926, 723. The reverse process, cholanolic acid  $\longrightarrow$  coprostane, has also been accomplished by the use of magnesium *isopropyl* iodide and subsequent reduction (H. Wieland and R. Jacobi, *Ber.*, 1926, **59**, [B], 1926; *A.*, 1926, 1139).

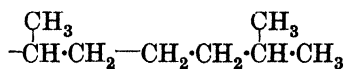


The complete elucidation of the nature of the side chain in the two sterols and the bile acids was effected last year by H. Wieland, O. Schlichting, and R. Jacobi.<sup>60</sup> By means of alternate Grignard condensations and oxidations, they were able to shorten the chain in cholanic acid one carbon atom at a time in the following manner until it was completely removed :

Cholanic acid ( $\text{C}_{24}$ )  $\longrightarrow$  norcholanic acid ( $\text{C}_{23}$ )  $\longrightarrow$  bisnorcholanic acid ( $\text{C}_{22}$ )  $\longrightarrow$  ætiocholyl methyl ketone ( $\text{C}_{21}$ )  $\longrightarrow$  ætiocholanic acid ( $\text{C}_{20}$ )  $\longrightarrow$  ætiocholanone ( $\text{C}_{19}$ , side-chain gone)  $\longrightarrow$  ætiobilanic acid ( $\text{C}_{19}$ , ring opened). These reactions can be formulated only in one way, namely, as follows :—



Incidentally these workers prepared cholane ( $\text{C}_{24}\text{H}_{42}$ ), the basic hydrocarbon of the bile-acid series, by Clemmensen-reduction of bisnorcholyl methyl ketone, which was obtained as a by-product in the second oxidation. Coprostan, which is  $\omega$ -isopropylcholane, therefore has the side-chain



the last five carbon atoms of which apparently represent an isoprene unit. Cholestane ( $\omega$ -isopropylallocholane) and cholesterol itself

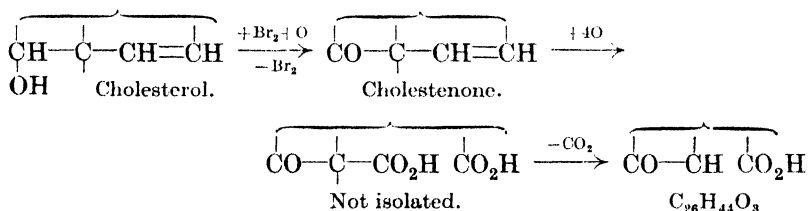
<sup>60</sup> *Z. physiol. Chem.*, 1926, **161**, 180; **A.**, 1926, 247.

must, of course, contain the same side chain. It is of interest in this connexion that five carbon atoms have been removed from cholesterol by chemical means,<sup>61</sup> with the production of a substance, "hypocholesterol" [side chain presumed to be  $-\text{CH}(\text{CH}_3)_2$ ], the properties of which are closely similar to those of cholesterol.

The attack on the tetracyclic  $\text{C}_{19}$ -ætiocolane nucleus has proceeded from two main directions. First, researches by Mauthner and Windaus extending over more than 30 years have yielded much information about that part of the cholesterol molecule which contains the hydroxyl group and double link. Secondly, the work of Wieland, Borsche, and others on cholic acid, carried out mainly in the last ten years, has extended the area of exploration, for this acid, owing to the distribution of its oxidisable centres, is susceptible of more varied types of degradation than is cholesterol. Latterly the study of hyodeoxycholic and lithocholic acids has brought about a fusion of these two lines of investigation. Finally, within the present year, the whole problem has entered upon a new phase represented by the application by Diels and his collaborators to cholesterol of the method of dehydrogenation to aromatic compounds.

The main points which have been established by degradation of cholesterol are as follows :

(1) The dibromide of cholesterol on oxidation yields a ketone from which, by removal of the bromine, cholestenone is formed; this on oxidation gives a  $\text{C}_{26}$ -ketonic acid, evidently by elimination of carbon dioxide from a  $\text{C}_{27}$ - $\beta$ -ketonic dibasic acid : <sup>62</sup>



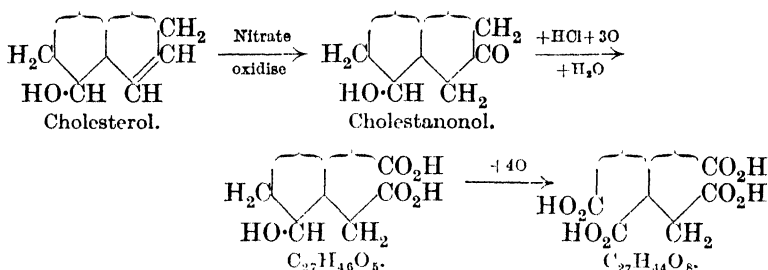
This proves that cholesterol is a  $\beta\gamma$ -unsaturated carbinol containing the group  $\cdot\text{CH}(\text{OH})\cdot\text{C}\cdot\text{CH}\cdot\text{CH}$ .

(2) When the nitro-derivative of cholesterol is oxidised, cholestanonol is formed (compare the conversion of indene into  $\beta$ -hydrindone), and this on conversion into the chloro-ketone, oxidation, and hydrolytic removal of the chlorine, yields a  $\text{C}_{27}$ -dibasic hydroxy-acid which on further oxidation gives a  $\text{C}_{27}$ -tetrabasic acid. This proves

<sup>61</sup> S. Fränkel and P. Dombacher, *Ber.*, 1927, **60**, [B], 1484; **A.**, 872.

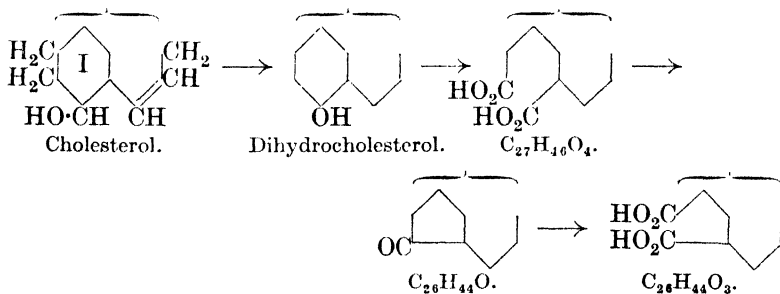
<sup>62</sup> *Ann. Reports*, 1917, **14**, 112.

that the carbinol and the ethenoid linkings in cholesterol must be in separate rings : <sup>63</sup>



Since the acid  $\text{C}_{27}\text{H}_{44}\text{O}_8$  is not a malonic acid, there must be a methylene group on the other side of the double link in cholesterol.

(3) When dihydrocholesterol is oxidised, a  $\text{C}_{27}$ -dibasic acid is formed which on heating loses carbon dioxide and water and yields a cyclic ketone; this on oxidation gives a  $\text{C}_{26}$ -dibasic acid which on heating loses water and forms a cyclic anhydride. Hence the  $\text{C}_{27}$ -acid is an adipic acid, and the  $\text{C}_{26}$ -acid a glutaric acid. It follows that the hydroxylated ring in cholesterol ("ring I") is a cyclohexane ring. <sup>64</sup> Also, two more methylene groups are diagnosed.

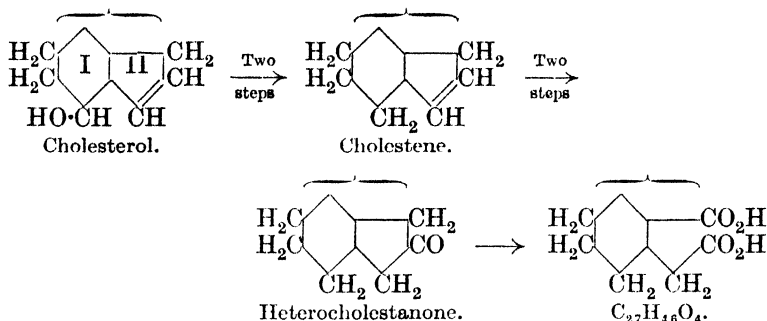


(4) Cholesteryl chloride on reduction by sodium and amyl alcohol yields cholestene, which may be converted through its nitro-derivative into heterocholestanone (7-cholestanone). On oxidation, this yields a  $\text{C}_{27}$ -dibasic acid, which on heating yields a cyclic anhydride and is evidently a glutaric acid. Hence the unsaturated ring in cholesterol (ring II) is a five-membered ring : <sup>65</sup>

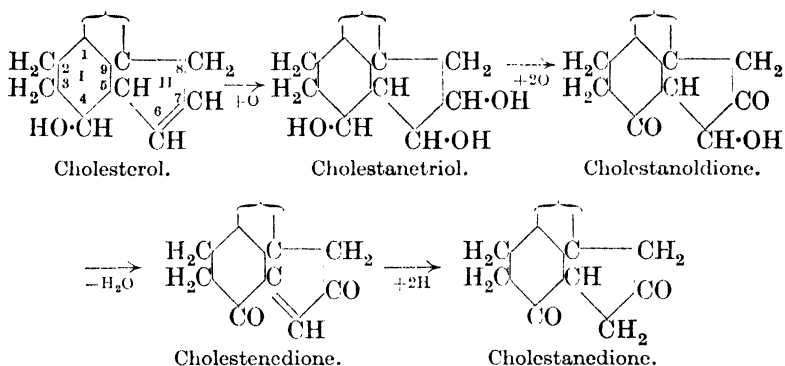
<sup>63</sup> A. Windaus and A. von Staden, *Ber.*, 1921, **54**, [B], 1059; *A.*, 1921, i, 507.

<sup>64</sup> A. Windaus and O. Dalmer, *ibid.*, 1919, **52**, [B], 162; *A.*, 1919, i, 203; A. Windaus, A. Rosenbach, and T. Riemann, *Z. physikal. Chem.*, 1923, **130**, 113; *A.*, 1923, i, 1204.

<sup>65</sup> A. Windaus and O. Dalmer, *loc. cit.*; A. Windaus, *Ber.*, 1920, **53**, [B], 488; *A.*, 1920, i, 434.



(5) Cholestanedione (4 : 7-) has been prepared from cholesterol in the following stages : <sup>66</sup>



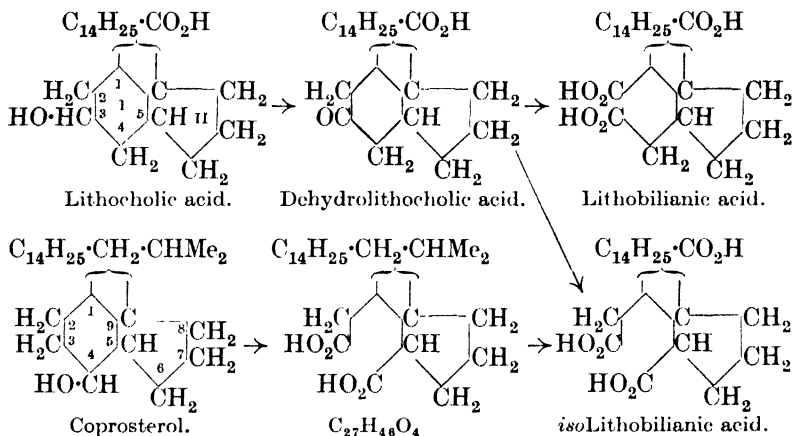
The same cholestanedione is obtained by oxidation of cholestanonol (see 2 above). This shows that it is the 4 : 7-diketone, and that the hydroxyl group which escapes oxidation in cholestanetriol is the centre one (6); from which it follows that the dehydration of cholestanoldione can occur only in one direction, and that therefore a hydrogen atom must be attached to the carbon atom ( $C_5$ ) between the carbinol group and the ethenoid group in cholesterol. All the valencies of  $C_5$  being thus accounted for, the remainder of the cholesterol molecule must be attached to rings I and II in the positions indicated in the formulæ.

The simplest of the bile acids is lithocholic acid, the investigation of which was commenced in 1920 by H. Wieland and P. Weyland.<sup>67</sup> It is a monohydroxycholanic acid,  $C_{24}H_{40}O_3$ . On oxidation, it is converted successively into the corresponding  $C_{24}$ -ketonic acid, dehydrolithocholic acid, and a mixture of two isomeric  $C_{24}$ -tribasic

<sup>66</sup> A. Windaus and E. Kirchner, *Ber.*, 1920, **53**, [B], 614; *A.*, 1920, i, 425.

<sup>67</sup> *Z. physiol. Chem.*, 1920, **110**, 123; *A.*, 1921, i, 178.

acids, lithobilianic acid and *isolithobilianic* acid. The second of these isomerides is identical with the acid obtained in 1923 by A. Windaus and T. Riemann<sup>68</sup> by a two-stage oxidation of coprosterol (the spatial isomeride of dihydrocholesterol). This proves that the ring which is hydroxylated in lithocholic acid is the same ring as that which bears the hydroxyl group in cholesterol (ring I), but that in lithocholic acid the group is in position 3 instead of position 4 :



[There are several reasons why lithobilianic and *isolithobilianic* acids are not spatial isomerides having the formula assigned to the latter, and of these the simplest is that this type of explanation is required to account for the formation from another bile acid of two more isomerides, one of which is obtainable by the oxidation of dihydrocholesterol. Still more convincing reasons emerge from the chemistry of deoxybilianic acid and bilianic acids (see below).]

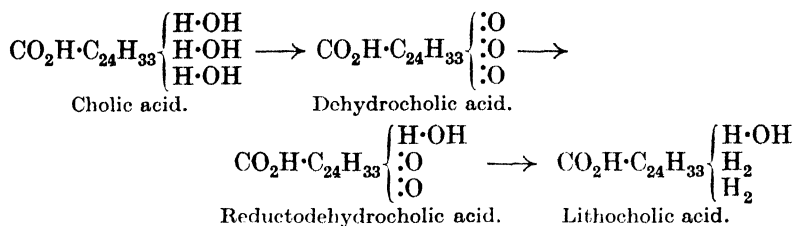
Further information respecting the nature of the residue  $C_{14}H_{25} \cdot CO_2H$  has been obtained by the combined study of deoxycholic acid (a dihydroxycholanolic acid) and of cholic acid (a trihydroxycholanolic acid). Oxidation of the latter produces the corresponding triketo-acid<sup>69</sup> (called "dehydrocholic acid," and in the earlier literature "dehydrocholanolic acid"), which on reduction by sodium amalgam yields the hydroxy-diketonic acid ("reducto-dehydrocholic acid").<sup>70</sup> The disemicarbazone of this on heating with sodium ethoxide (Wolff's reaction) gives lithocholic acid :<sup>71</sup>

<sup>68</sup> *Z. physiol. Chem.*, 1923, **126**, 227; *A.*, 1923, i, 567.

<sup>69</sup> O. Hammersten, *Ber.*, 1881, **14**, 71; *A.*, 1881, 624.

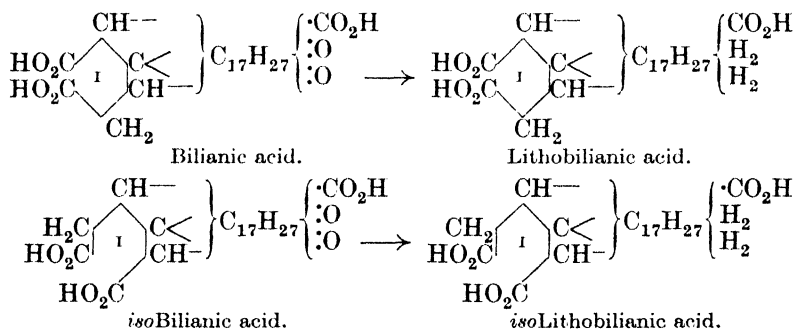
<sup>70</sup> M. Schenk, *Z. physiol. Chem.*, 1909, **63**, 308; *A.*, 1910, i, 10.

<sup>71</sup> W. Borsche and F. Hallwas, *Ber.*, 1922, **55**, [B], 3318, 3324; *A.*, 1922, i, 1158, 1159.



This shows that one hydroxyl group in cholic acid is in ring I and in position 3.

Just as dehydrolithocholic acid on oxidation yields a mixture of lithobilianic and *isolithobilianic* acids, so also the triketo-acid (dehydrocholic acid) gives a mixture of bilianic and *isobilianic* acids through the fission of one ring.<sup>72</sup> That these acids are indeed the diketo-derivatives of the corresponding acids of the litho-series is proved by the observation that they can be converted into the respective carbonyl-free acids by Wolff's method.<sup>71, 73</sup> It is therefore ring I which has been opened in the formation of bilianic and *isobilianic* acids.



By the use of milder conditions it has been found possible to reduce one of the carbonyl groups in bilianic and *isobilianic* acids and leave the other intact. Now deoxycholic acid on oxidation with chromic acid yields the corresponding diketo-acid ("dehydrodeoxycholic acid"), and this on further oxidation with nitric acid gives a mixture of tribasic ketonic acids, deoxybilianic and *iso-deoxybilianic* acids,<sup>74</sup> respectively identical with the products of mild reduction of bilianic and *isobilianic* acids. Here again, there-

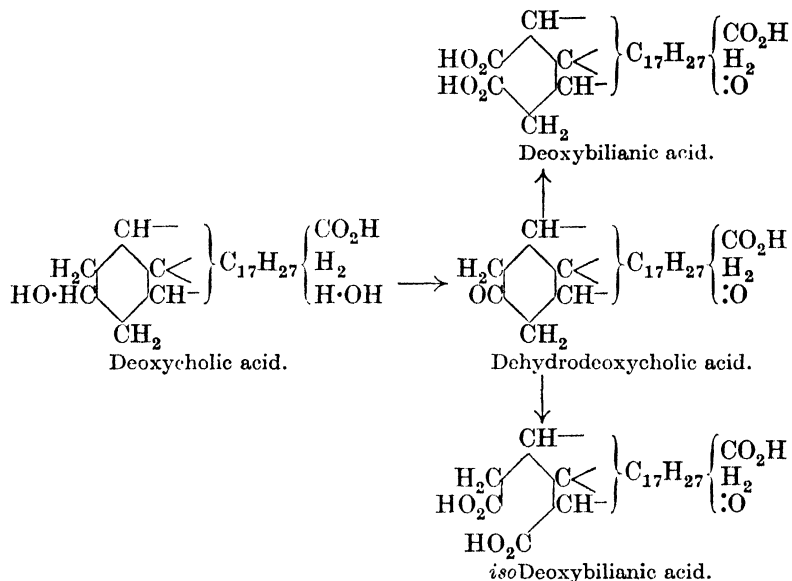
<sup>72</sup> F. Pregl, *Monatsh.*, 1903, **24**, 19; *A.*, 1903, i, 318.

<sup>73</sup> W. Borsche and H. Behr, *Nachr. Ges. Wiss. Göttingen*, 1920, 188; *A.*, 1921, i, 729.

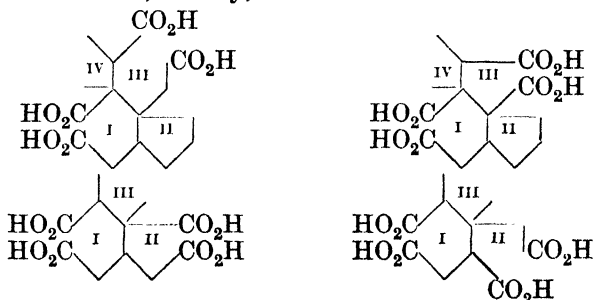
<sup>74</sup> H. Wieland and A. Kulenkampff, *Z. physiol. Chem.*, 1920, **108**, 295; *A.*, 1921, i, 112.



fore, it is ring I which has opened; from which it follows that one hydroxyl group in deoxycholic acid is also in position 3.



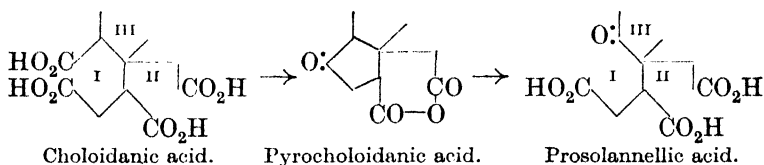
On further oxidation of deoxybibilanic acid a second ring, that containing the carbonyl group, is opened (+ 3O), and the product, choloidanic acid,  $\text{C}_{24}\text{H}_{36}\text{O}_{10}$ , on heating loses carbon dioxide and water and yields pyrocholoidanic acid,  $\text{C}_{23}\text{H}_{32}\text{O}_6$ , in the formation of which two new rings have been produced, a ketone ring and an anhydride ring.<sup>75</sup> Choloidanic acid therefore contains an adipic or pimelic acid residue, and, independently of this, a succinic or glutaric acid residue; further, it cannot contain a malonic acid residue.<sup>76</sup> Having regard to the information yielded by the investigation of cholesterol, there are at first sight four possible formulæ for choloidanic acid, namely,



<sup>75</sup> H. Wieland, *Z. physiol. Chem.*, 1920, **108**, 306; *A.*, 1921, i, 113.

<sup>76</sup> *Idem, ibid.*, 1927, **167**, 70; *A.*, 767.

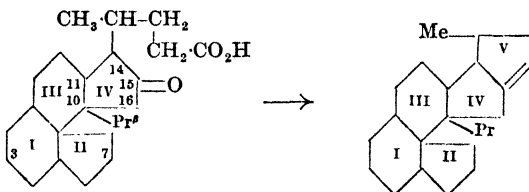
but of these only the fourth is consistent with the properties of the acid formed by hydrating the anhydride ring in pyrocholoidanic acid. The acid thus obtained on further oxidation takes up *two* atoms of oxygen, yielding a tetrabasic ketonic acid,  $C_{23}H_{34}O_9$ , which is not a  $\beta$ -ketonic acid.<sup>77</sup> In the formation of this acid the carbonyl ring of pyrocholoidanic acid has opened in such a way as to introduce a carbonyl group into a new ring, that is, a ring which is not one of the two hydroxylated rings in deoxycholic acid. The fact that this product, prosolannellic acid, is not a  $\beta$ -ketonic acid determines the formulæ of choloidanic and pyrocholoidanic acids :



This proves<sup>78</sup> that the second hydroxyl group in deoxycholic acid is in ring II, and in one of the positions 6 and 7. But deoxybilanic acid on heating forms pyrodeoxybilanic acid,  $C_{23}H_{34}O_4$ , and this on oxidation yields a pentabasic acid, norcholoidanic,  $C_{23}H_{34}O_{10}$ , which is not a malonic acid. This shows that ring II in pyrodeoxybilanic

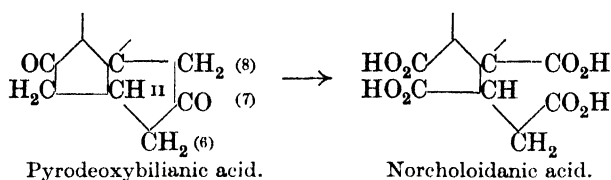
<sup>77</sup> H. Wieland and W. Schulenberg, *Z. physiol. Chem.*, 1922, **126**, 232; *A.*, 1922, i, 838.

<sup>78</sup> It is not apparent to the Reporter why ring IV is not considered to have opened between  $C_{15}$  and  $C_{16}$  (formula below) in the formation of choloidanic acid. The necessary implications would be (i) that ring IV must be five-membered, (ii) that the second hydroxyl group in deoxycholic and cholic acids is at  $C_{15}$  (or perhaps  $C_{16}$ ) instead of  $C_7$ , (iii) that the carboxylated side chain is at  $C_{14}$ , and (iv) that the (*iso*-?) propyl group is at  $C_{10}$  (or perhaps  $C_{11}$ ). A natural explanation would then be possible for such facts as the formation of a pentacyclic unsaturated ketone  $C_{22}H_{32}O$  (W. Borsche, *Ber.*, 1924, **57**, [B], 1435; *A.*, 1924, i, 1201; H. Wieland, *Z. physiol. Chem.*, 1925, **142**, 191; *A.*, 1925, i, 1065) from pyrodeoxybilanic acid, and of an unsaturated hydrocarbon  $C_{23}H_{36}$  from the "7-ketocholanic acid" (H. Wieland and O. Schlichting, *ibid.*, 1925, **150**, 267; *A.*, 1926, 400) obtained from isolithocholic acid (p. 141), and other similar observations recorded by Wieland (*loc. cit.*) under the title "Some Unexplained Results":

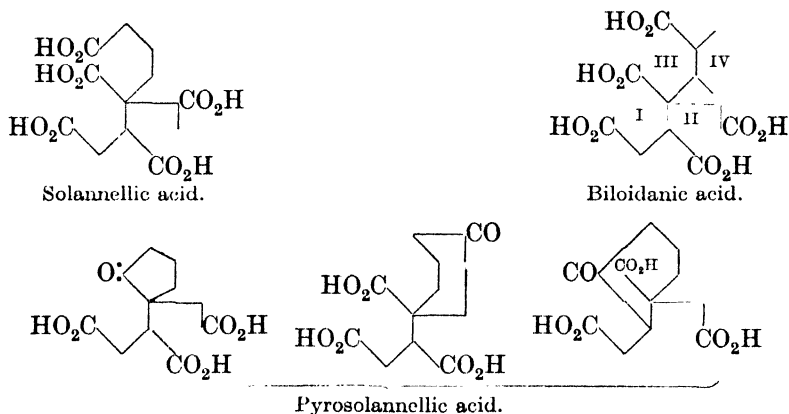


For the purposes of the above account, which is based on the conclusions reached by the workers concerned, this possibility is disregarded, since it may be excluded by considerations which have not yet been disclosed.

acid must have opened between carbon atoms 7 and 8, so that the second hydroxyl group in deoxycholic acid is in position 7 : <sup>79</sup>



Prosolanelllic acid is the real starting point of the investigation into the nature of ring III.<sup>80</sup> On oxidation with nitric acid, ring III opens and solannellic acid, a hexabasic acid,  $C_{23}H_{34}O_{12}$ , is produced. This on heating gives pyrosolanelllic acid,  $C_{22}H_{32}O_9$ , for which, again, there are apparently four possible formulæ. One of these can be excluded on the ground that the acid, biloidanic acid ("norsolanelllic acid,"  $C_{22}H_{32}O_{12}$ ), formed on oxidation is not a malonic acid.<sup>81</sup> The same limitation settles any possible ambiguity as to the direction of fission of the other three possible structures (below) for pyrosolanelllic acid, and it happens that all of them lead to the same formula for biloidanic acid :



This formula shows that ring III of the ætiocholane nucleus must be a cyclohexane ring<sup>82</sup> and that ring IV can be attached to it

<sup>79</sup> H. Wieland and F. Adickes, *Z. physiol. Chem.*, 1922, **120**, 232; *A.*, 1922, i, 838.

<sup>80</sup> H. Wieland and W. Schulenberg, *loc. cit.*

<sup>81</sup> *Idem*, *Z. physiol. Chem.*, 1922, **132**, 213; *A.*, 1923, i, 41; H. Wieland, *ibid.*, 1927, **167**, 70; *A.*, 767; W. Borsche and R. Frank, *Ber.*, 1927, **60**, [B], 723; *A.*, 459.

<sup>82</sup> If the improbable assumption of a *spiro*-union between rings III and IV is excluded.

only in the position shown. The formula of prosolannellic acid shows that a hydrogen atom is attached to position 1 in ring I, and it is also evident that the next three positions in ring III must be occupied by methylene groups.

It is now possible to consider the constitution of cholic acid in greater detail. The reduction of bilianic acid to deoxybilianic acid (and of isobilianic acid to isodeoxybilianic acid) shows that two of the three hydroxyl groups in cholic acid are located in positions 3 and 7.<sup>83</sup> That the third hydroxyl group is in ring III is proved by the fact that bilianic acid may be directly oxidised to biloidanic acid.<sup>84</sup> Since the hydroxyl group is secondary, there are two available positions, namely 12 and 13 (numbered formula on p. 140); and the decision between these depends on the investigation of chenodeoxycholic acid.

Chenodeoxycholic acid,  $C_{24}H_{40}O_4$ , is a dihydroxycholanolic acid, and on oxidation gives the corresponding diketo-acid, dehydrochenodeoxycholic acid,  $C_{24}H_{36}O_4$ .<sup>85</sup> This has been reduced to lithocholic acid,<sup>86</sup> which proves that one hydroxyl group in chenodeoxycholic acid is in position 3. The diketo-acid on further oxidation gives chenodeoxybilianic acid,  $C_{24}H_{36}O_7$ ,<sup>87</sup> which on reduction by Clemmensen's method yields lithobilianic acid.<sup>88</sup> This shows that in the formation of chenodeoxybilianic acid ring I has been broken in the direction shown in the formulæ (below). Chenodeoxybilianic acid still contains one carbonyl group, and on reduction it forms the hydroxy-acid, which at once passes into a very stable  $\gamma$ -lactonic acid, chenodeoxybiliobanic acid ("deoxybiliobanic acid"),  $C_{24}H_{36}O_6$ .<sup>89</sup> The same lactonic acid is obtained by directly oxidising chenodeoxycholic acid with alkaline hypobromite.<sup>90</sup> These relationships show that the second hydroxyl group in chenodeoxycholic acid must be in one of the positions 6, 8, and 12:

<sup>83</sup> Compare F. Boedecker and H. Volk, *Ber.*, 1922, **55**, [B], 2302; *A.*, 1922, i, 1027.

<sup>84</sup> M. Schenk, *Z. physiol. Chem.*, 1920, **110**, 167; *A.*, 1921, i, 179; H. Wieland and O. Schlichting, *ibid.*, 1922, **119**, 76, 213; *A.*, 1922, i, 554; *A.*, 1923, i, 41.

<sup>85</sup> A. Windaus, A. Bohne, and E. Schwarzkopf, *loc. cit.*

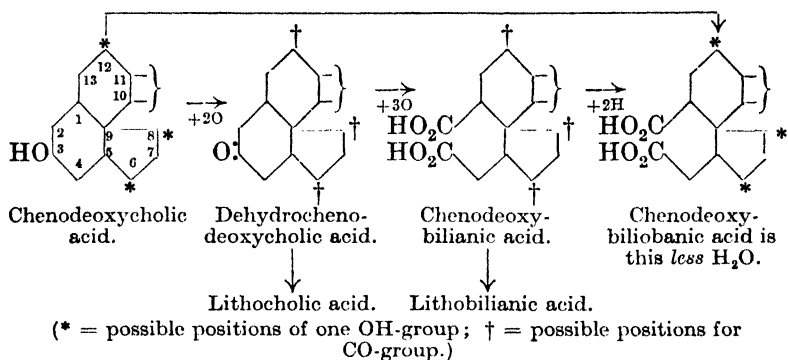
<sup>86</sup> A. Wieland and R. Jacobi, *Z. physiol. Chem.*, 1925, **148**, 232; *A.*, 1925, i, 1488.

<sup>87</sup> A. Windaus, A. Bohne, and E. Schwarzkopf, *loc. cit.*; A. Windaus and A. van Schoor, *Z. physiol. Chem.*, 1926, **157**, 177; *A.*, 1927, 56.

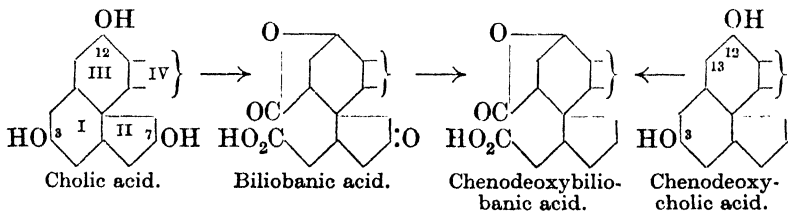
<sup>88</sup> *Idem*, *ibid.*

<sup>89</sup> A. van Schoor. Unpublished observation referred to by W. Bors he and R. Frank, *Ber.*, 1926, **59**, [B], 1749.

<sup>90</sup> A. Windaus and A. van Schoor, *Z. physiol. Chem.*, 1925, **148**, 225; *A.*, 1926, 169.



(If it were assumed that chenodeoxybilibanic acid were a  $\delta$ -lactonic acid, then chenodeoxycholic acid would be a 3 : 7-dihydroxycholanolic acid, and identical with, or only spatially different from, deoxycholic acid. The latter has, however, very different properties and it is noteworthy that it has never been converted into a deoxybilibanic acid.) Now cholic acid on oxidation by alkaline hypobromite yields bilibanic acid,<sup>91</sup>  $\text{C}_{24}\text{H}_{34}\text{O}_7$ , the lactonic acid of a hydroxy-keto-tribasic acid.<sup>92</sup> Reduction of bilibanic acid (tribasic diketolactonic acid) gives the same lactonic acid,<sup>93</sup> and this on reduction of the carbonyl group to a methylene group gives chenodeoxybilibanic acid.<sup>94</sup> This proves, first, that ring I has opened in the formation of bilibanic acid exactly as in the formation of chenodeoxybilibanic acid; and, secondly, that the potential hydroxyl group in chenodeoxybilibanic acid is in one of the only positions outside ring I which are, or might be, hydroxylated in cholic acid, namely 7, 12, and 13 (p. 139). But this potential hydroxyl group must also be in one of the positions 6, 8, and 12 (p. 139). Hence chenodeoxycholic acid is 3 : 12-dihydroxycholanolic acid and cholic acid is 3 : 7 : 12-trihydroxycholanolic acid.



This orientation of the third hydroxyl group in cholic acid is consistent with the circumstance that the 3 : 13-dihydroxy-isomeride of chenodeoxycholic acid is known in both stereochemical forms

<sup>91</sup> H. Wieland and L. Fukelman, *Z. physiol. Chem.*, 1923, **140**, 144; *A.*, 1923, i, 1205.

<sup>92</sup> W. Borsche and R. Frank, *Ber.*, 1926, **59**, [B], 1748; *A.*, 1926, 1140.

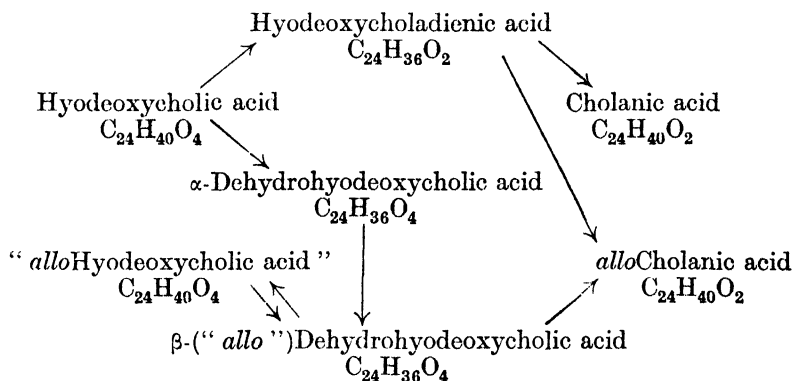
<sup>93</sup> *Idem*, *ibid.*

<sup>94</sup> *Idem*, *ibid.*

(one of them is hydoexychohic acid); and in passing it may be noted that a 7 : 12-dihydroxycholanolic acid ("isodeoxychohic acid"), not identical with any known natural product, has been prepared by an indirect reduction of the 3-hydroxyl group in cholic acid.<sup>95</sup> 7-Hydroxycholanolic acid ("isolithocholic acid") has also been made by indirect reduction of deoxychohic acid; it also is not known as a natural product.<sup>96</sup>

It is now necessary to review the nature of the stereoisomerism between dihydrocholesterol and coprosterol or cholanolic and *allo*-cholanolic acids, for recent researches on hydoexychohic acid have shown this to be located in the decahydronaphthalene residue represented by rings I and III.

Hydoexychohic acid is a dihydroxy-acid. On dehydration it yields hydoexycholadienic acid, which on catalytic reduction gives a mixture of cholanolic and *allo*cholanolic acids.<sup>97</sup> On cautious oxidation hydoexychohic acid yields the corresponding diketo-acid,  $\alpha$ -dehydrohydoexychohic acid, which, however, is unstable and on treatment with acids, alkalis or warm solvents passes into its  $\beta$ -stereoisomeride. The latter, on reduction by Clemmensen's method, yields *allo*cholanolic acid exclusively,<sup>98</sup> and on mild reduction gives an isomeride of natural hydoexychohic acid, from which isomeride it can be directly reproduced by oxidation.<sup>59</sup> It is therefore evident that natural hydoexychohic acid belongs to the cholanolic, and not to the "*allo*"-series, but that, for a reason yet to be given, certain of its derivatives possess a marked tendency to stereochemical inversion :



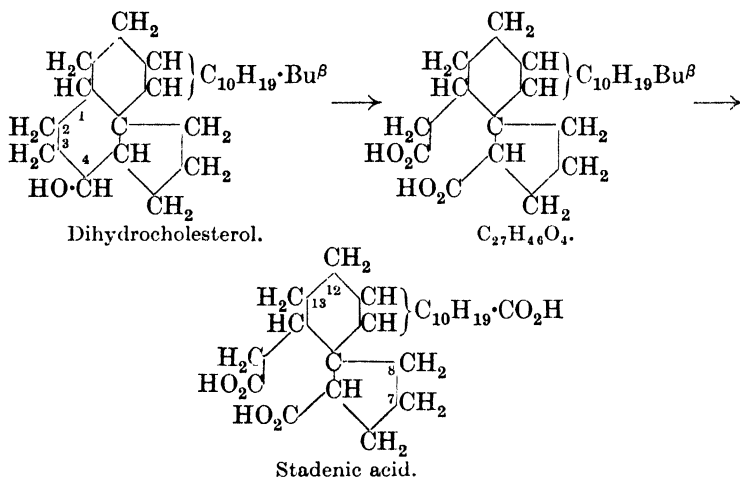
<sup>95</sup> H. Wieland, E. Honold, and J. Pascual-Vila, *Z. physiol. Chem.*, 1923, **130**, 326; *A.*, 1923, i, 1206; J. Pascual-Vila, *Anal. Fís. Quím.*, 1923, **21**, 390; *A.*, 1924, i, 47.

<sup>96</sup> H. Wieland and O. Schlichting, *Z. physiol. Chem.*, 1925, **150**, 267; *A.*, 1926, 400; M. Schenk and H. Kirchhof, *ibid.*, 1927, **163**, 120; *A.*, 1927, 562.

<sup>97</sup> A. Windaus and A. Böhne, *Annalen*, 1923, **433**, 278; *A.*, 1924, i, 47.

<sup>98</sup> A. Windaus, *Z. angew. Chem.*, 1923, **36**, 309; *A.*, 1923, i, 922.

On further oxidation of  $\beta$ -hydroxycholeic acid a tribasic monoketo-acid,  $C_{24}H_{36}O_7$ , known as ketostadenic acid, is formed, and it is evident that one of the two ketonic rings in the " $\beta$ -acid" has been opened. When the remaining ketonic group is reduced to methylene by Wolff's method, two isomeric acids are formed, one of which is the known *isolithobilianic acid*, and the other, *stadenic acid*, is a stereoisomeride of this, because it has been prepared (by Staden—hence its name) from dihydrocholesterol<sup>99</sup> just as *isolithobilianic acid* has been prepared from coprosterol:



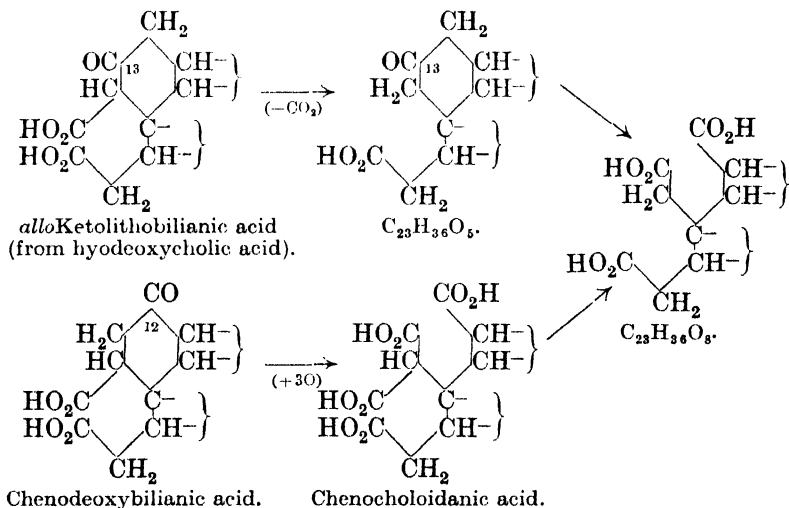
It follows that one hydroxyl group in hydoxycholeic acid must be in either of positions 3 and 4.

Next, hydoxycholeic acid when oxidised by hypobromite yields an acid,  $C_{24}H_{38}O_7$ , known as hydroxylithobilianic acid, in the production of which one hydroxyl-bearing ring has opened and the other hydroxyl group has survived. The product, on reduction with hydriodic acid in acetic acid (replacement of OH by H), yields the known lithobilianic acid. The stereoisomeride, *allolithobilianic*, is produced if the hydroxylithobilianic acid, instead of being directly reduced, is dehydrated to lithobilienic acid,  $C_{24}H_{36}O_6$ , which is then reduced; and the proof that lithobilianic and *allolithobilianic* acids are stereoisomerides is that on heating they yield the same "*pyro-acid*" (monobasic ketonic acid),  $C_{23}H_{36}O_3$ . From the structure of lithobilianic acid it follows that the hydroxyl group of ring I in hydoxycholeic acid must be in either of positions 2 and 3. Hence it is in position 3, just as in all the other natural cholane acids.<sup>59</sup>

<sup>99</sup> A. Windaus, H. Grimm, and A. von Staden, *Z. physiol. Chem.*, 1921, 117, 146; *A.*, 1922, i, 541.

The methyl ester of ketostadenic acid undergoes a remarkable reaction on heating: it splits off methyl alcohol and passes into the ester of an enol-lactone, and this behaviour is not reproduced by the esters of deoxybilianic, *isodeoxybilianic* and *chenodeoxybilianic* acids.<sup>97</sup> It follows (compare formula of stadenic acid, above) that the second hydroxyl group in hyodeoxycholic acid is either in position 13, or, perhaps, in position 8.

Finally, hydroxylithobilianic acid (in which carboxyl groups occupy the positions which were originally 2 and 3) on mild oxidation gives ketolithobilianic, which, like  $\alpha$ -dehydrohyodeoxycholic acid, is unstable, and passes on contact with warm acids into the *allo*-stereoisomeride (the assumed configuration of which is confirmed by its reduction to *allolithobilianic* acid). *allo*Ketolithobilianic acid is a  $\beta$ -ketonic acid, since it readily loses carbon dioxide, yielding the keto-dicarboxylic acid  $C_{23}H_{36}O_5$ . It follows that hyodeoxycholic acid must be 3 : 13-dihydroxycholanolic acid :



Its relation to chenodeoxycholic acid (3 : 12-dihydroxycholanolic acid) confirms this orientation. The above dibasic keto-acid  $C_{23}H_{36}O_5$  on oxidation behaves normally, yielding a tetrabasic acid,  $C_{23}H_{36}O_8$ .<sup>1</sup> Chenodeoxybilianic acid,  $C_{24}H_{36}O_7$ , on oxidation yields chenocholoidanic acid,  $C_{24}H_{36}O_{10}$ , which is a malonic acid, and on heating gives the same tetrabasic acid<sup>2</sup> (formulae above).

Now when in the light of the above orientation the degradations of hyodeoxycholic acid are expressed by formulae, two points

<sup>1</sup> A. Windaus and A. van Schoor, *Z. physiol. Chem.*, 1926, **157**, 177; **A.**, 1927, 56.

<sup>2</sup> H. Wieland and R. Jacobi, *ibid.*, 1925, **148**, 232.

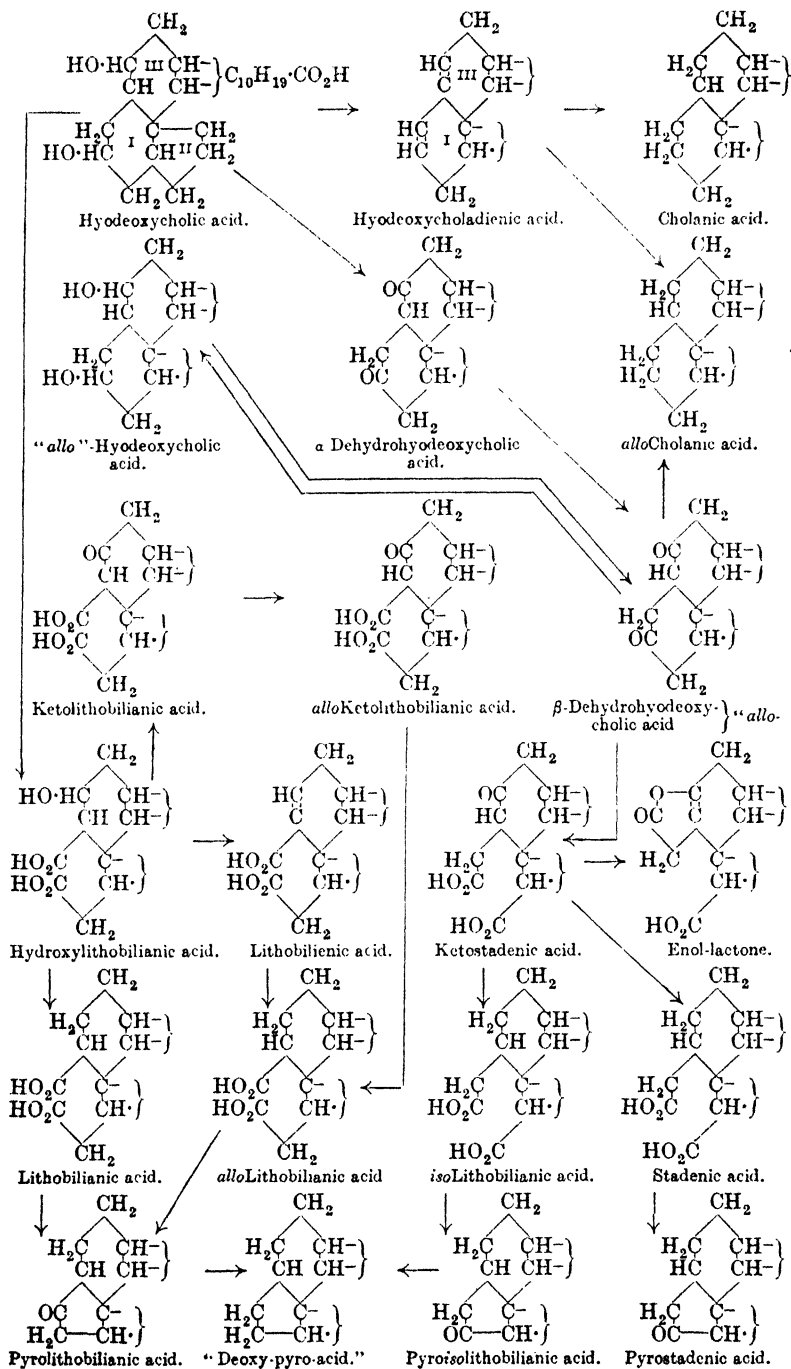


emerge. First, facile transformation from the cholane series to the *allo*-series is seen to occur only when a double bond can become attached to  $C_1$ , e.g., by the enolisation of a neighbouring carbonyl group; secondly, the formation of a spatially inverted product of decomposition, or of two stereoisomerides, occurs only (a) in the above circumstances, or (b) if a double bond is actually attached to  $C_1$  (see tabular summary on p. 145). It follows that the two series are to be regarded the one as *cis*- and the other as *trans*-decahydro-naphthalene derivatives, and that the peculiar behaviour of hyodeoxycholic acid in yielding stereoisomerides is attributable to the particular orientation of the hydroxyl group in ring III.

One further observation, namely, that pyrolithobilianic and pyroisolithobilianic acids yield the same "deoxy-pyro-acid" on reduction (tabular summary, bottom), determines the "probable" configurations of the two series. Lithobilianic and *allolithobilianic* acids yield the same pyro-acid, and it is therefore assumed that whichever was *trans*- has undergone inversion in the formation of the new five-ring. *iso*Lithobilianic and stadenic acids (in which no carbonyl group is directly attached to  $C_1$ ) each yield their own pyro-acids, which therefore retain the respective configurations of the parent acids. Since in any event the common pyro-acid of lithobilianic and *allolithobilianic* acids is regarded as *cis*-, the identity of its deoxy-pyro-acid with that of pyroisolithobilianic acid shows that *isolithobilianic* acid is *cis*-, and that its isomeride, stadenic acid, is *trans*-. Hence coprosterol and the five bile acids are *cis*- ("cholane series"), and cholesterol is *trans*- ("allocholane series"). In the formulæ of the tabular summary the hydrogen atom attached to  $C_1$  has been placed on the same side of  $C_1$  as ring II when this hydrogen atom and ring II are assumed to be in *cis*-positions with respect to the decahydronaphthalene skeleton, and on the opposite side to ring II when they are assumed to be in *trans*-positions. This interpretation, which is that of the authors, clearly depends on the supposition that the *cis*-configuration is the more stable when a five-membered ring replaces ring I—a point in regard to which some might, for the present, wish to keep an open mind. It is also obvious that the complete cholesterol molecule may contain possibilities of stereoisomerism other than that of the *cis-trans*-decalene type in rings I and III. A. Windaus<sup>3</sup> has converted cholesterol into "*allocholesterol*," which shows a marked tendency to pass back into cholesterol, and on reduction yields coprosterol.

Step-by-step degradation of the cholane skeleton has not yet penetrated far into ring IV, although now that *ætiocholanone* has

<sup>3</sup> *Annalen*, 1927, 453, 101; A., 557.



been prepared (p. 130) a detailed examination of this ring (starting from the other side) will doubtless soon be made. Nevertheless the formation of this ketone and of aetiobilanic acid gives a certain amount of definite information, namely, that no other side chain is attached to the carbon atom which bears the carboxylated side chain in cholanic acid, and that this carbon atom is adjacent to a methylene group. Furthermore, ring IV must contain any side chains which are present in cholane, since the valencies of every carbon atom in rings I, II and III (except those common to rings III and IV) have been fully accounted for. It therefore follows from the compositions of the substances that if ring IV is a 5-ring it must carry, in addition to the long chain, a propyl group or its equivalent; and that if it is a 6-ring it must bear an ethyl group or two methyl groups.

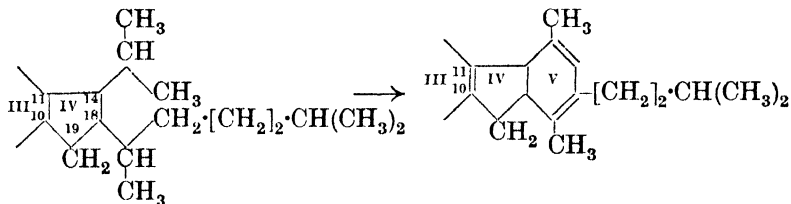
Some evidence with regard to these questions has come, rather unexpectedly, from another direction. Early in the year O. Diels and W. Gädke showed <sup>4</sup> that on dehydrogenating cholesterol with hot palladised charcoal chrysene is produced in considerable amount. If the conclusions based on detailed degradation are correct, the production of chrysene must involve a re-arrangement of the carbon skeleton, possibly of some such kind as *cyclopentane* compounds are known (Zelinsky) to undergo at high temperature in the presence of surface catalysts; it therefore became important to attempt dehydrogenation under milder conditions. A paper has just appeared <sup>5</sup> in which this has been done by the use of selenium at 240—310°. Cholesteryl chloride was used instead of cholesterol and two aromatic hydrocarbons,  $C_{25}H_{24}$  and  $C_{18}H_{16}$ , were isolated.

The former of these can readily be dinitrated, and on oxidation forms a coloured ketone,  $C_{25}H_{22}O$ , reducible to an alcohol,  $C_{25}H_{24}O$ . This indicates the presence of a fluorene nucleus, that is to say, of a five-membered ring. Now the ketonic acid,  $C_{26}H_{44}O_3$ , obtained by Windaus by oxidation of cholestenone (p. 131), on reduction by Clemmensen's method, yields a monobasic acid,  $C_{26}H_{46}O_2$ , in which ring II is absent; and this acid on dehydrogenation with selenium gives a hydrocarbon,  $C_{24}H_{26}$ , which exhibits precisely similar indications of a fluorene structure. Thus it cannot be ring II, and therefore it is probably ring IV, which is the source of the 5-ring in these hydrocarbons. This is a far-reaching conclusion, because it implies that the additional ring ("ring V") which, from their composition, these hydrocarbons must contain, is produced from the side chains attached to ring IV. Least difficulty was experienced in formulating the course of the decompositions

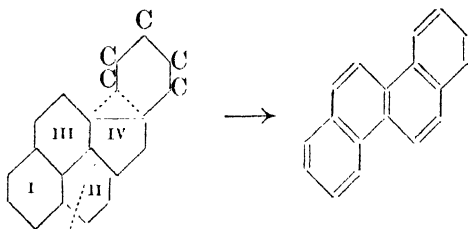
<sup>4</sup> *Ber.*, 1927, **60**, [B], 140; *A.*, 241.

<sup>5</sup> O. Diels, W. Gädke, and P. Körding, *Annalen*, 1927, **459**, 1.

by assuming that two side chains, *isooctyl* and *isopropyl*, are in adjacent positions and interact. Since the *isooctyl* group is also adjacent to a methylene group (above), it must, according to this assumption, be located in position 18, and the *isopropyl* group must therefore occupy either of positions 14 and 19. Reasons (not, however, of a perfectly convincing kind) are given for preferring the former orientation, and the production of the fluorene skeleton is formulated thus :



On this basis formulæ can readily be developed for the hydrocarbons isolated ( $C_{18}H_{16}$  is regarded as an indene formed with elimination of the *isooctyl* side chain), and the production of chrysene may be explained by assuming that at the high temperature of dehydrogenation with palladised charcoal ring II is completely eliminated and that ring IV is converted into a 6-ring by the fission (at  $C_{18}$ ) and subsequent closure of ring V :



Admittedly this argument is not conclusive ; nevertheless it seems to provide a possible picture of ring IV and its attachments pending their detailed investigation.

The above simplified account makes reference only to the smallest selection of experimental material on the basis of which the conclusions which have been reached with regard to the structures of the cholane group of compounds might be justified ; and it will be realised that this constitutes only a very small proportion of the degradations of these compounds which have been carried out by Windaus, Wieland, and Borsche, whose combined work already represents one of the most remarkable constitutional investigations that have ever adorned Organic Chemistry. It should also be stated that the order here adopted is only very roughly the historical order ; for the historical development is much too complex (and

is rendered more so by a continually changing nomenclature) for reproduction within a small compass. As nearly always happens, incorrect conclusions have been reached, and then modified with consequential wholesale readjustments; correct inferences have been first guessed, and subsequently proved; circuitous, and sometimes highly doubtful arguments have had to serve until simple and direct proof became available. As long ago as 1918 Windaus proposed a cholesterol formula not very different from that now advocated by Diels, Gädke, and Körding, and last year Wieland, Schlichting, and Jacobi advanced one even more closely similar.

In view of the established relation between ergosterol and vitamin-*D* and of the suspicion that the phytosterols (or some of them) may represent bio-synthetic sources of cholesterol and hence indirectly of coprosterol and the bile acids, it is probable that the investigation of the vegetable sterols will form a prominent feature of future work in this field.

Such work has already been begun. Sitosterol,  $C_{27}H_{46}O$ , is extremely similar to cholesterol and is isomeric with it. Like cholesterol, it contains one hydroxyl group, one double bond and four rings. By methods precisely similar to those used in the case of cholesterol it has been shown<sup>6</sup> that the hydroxyl group is contained in a 6-membered, and the double bond in a 5-membered, ring. Since sitosterol, like cholesterol, yields acetone on energetic oxidation, it is probable that an *isopropyl* group terminates the side chain. Yet none of the products obtained from sitosterol, even sitostane, the fully reduced hydrocarbon, is identical with any known product derived from cholesterol or coprosterol. Ergosterol (from yeast),  $C_{27}H_{42}O$ , contains four rings, a hydroxyl group, and three double bonds. On complete reduction it yields ergostane, which is isomeric, but not identical, with cholestane, coprostane, and sitostane,  $C_{27}H_{48}$ .<sup>7</sup> Stigmasterol,  $C_{30}H_{50}O$ , is a higher sterol; it contains four rings, a hydroxyl group, and two double bonds; and the hydroxyl group is known to be contained in a 6-membered ring. Complete reduction yields stigmastane,  $C_{30}H_{54}$ .<sup>8</sup> Several other plant sterols are known, but their investigation has as yet scarcely been begun.

#### *Benzene Derivatives. Orientation and Related Topics.*

*Genesis of Orienting Effects.*—This subject was dealt with at some length in last year's Report, but two additional points

<sup>6</sup> A. Windaus and E. Rahlén, *Z. physiol. Chem.*, 1918, **101**, 223; *A.*, 1918, i, 338; A. Windaus and J. Brunken, *ibid.*, 1924, **140**, 52; *A.*, 1925, i, 394.

<sup>7</sup> A. Windaus and W. Grosskopf, *ibid.*, 1922, **124**, 8; *A.*, 1923, i, 75.

<sup>8</sup> A. Windaus and J. Brunken, *ibid.*, 1924, **140**, 47; *A.*, 1925, i, 394.

which have been emphasised in the year under review require reference.

(i) *Ammonium salts*. It was pointed out by F. R. Goss, C. K. Ingold, and I. S. Wilson that, on the modern theory of strong electrolytes, the electrostriction of the ions in aromatic ammonium salts must reduce the proportion of meta-substitution, which would therefore be smaller the greater the ionic concentration;<sup>9</sup> they suggested also that this effect would be assisted in the salts of primary, secondary, and tertiary bases by the co-ordination of the anion through hydrogen,<sup>10</sup> thus accounting for the generally smaller degree of *m*-nitration exhibited by primary, secondary, and tertiary benzylamines than by the quaternary compounds. (A similar effect has since been observed in the  $\beta$ -phenylethylamine series.)<sup>11</sup> B. Flürscheim and E. L. Holmes first showed<sup>12</sup> that the proportion of *m*-derivative formed on nitrating a benzylamine in sulphuric acid could be considerably decreased if the ionic concentration were increased by saturating the solution with ammonium sulphate. They attributed the result to increased association between the ions. These observations have now been extended by A. Pollard and R. Robinson,<sup>13</sup> who, by the use of more soluble sulphates, have observed still larger depressions in the proportion of *m*-substitution. The latter authors discuss some of the structural influences which might affect the degree of electrostriction under given physical conditions, and point out that ring-closure between the groups attached to the charged nitrogen atom must be an important factor, since it increases the rigidity of the molecular framework and thus resists the alteration of the angles between the groups which must occur when the anion closely approaches the central atom. In this way they account for the notably higher proportion of *m*-nitro-derivative given by benzylpiperidine than by benzyldiethylamine.

(ii) *Carbonyl compounds*. The influence of an attached carbonyl group on the *op*-directive power of a phenoxy oxygen atom (as in  $R \cdot CO \cdot O \cdot C_6H_5$ ), or anilino-nitrogen atom, was discussed in last year's Report<sup>14</sup> in terms of the conception (I) that the process (*b*), actuated by (*a*), competes with the process (*x*) to which the *op*-directing action of the group is due; or, in other words, that the

<sup>9</sup> *J.*, 1926, 2440; *A.*, 1926, 1132.

<sup>10</sup> T. S. Moore, *J.*, 1912, 101. 1673; W. M. Latimer and W. H. Rodebush, *J. Amer. Chem. Soc.*, 1920, 42, 1419; *A.*, 1920, ii, 537.

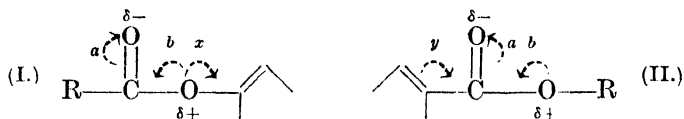
<sup>11</sup> F. R. Goss, W. Hanhart, and C. K. Ingold, *J.*, 1927, 250; *A.*, 236.

<sup>12</sup> *J.*, 1926, 1562; *A.*, 1926, 830.

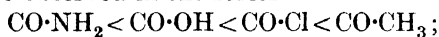
<sup>13</sup> *J.*, 1927, 2770.

<sup>14</sup> *Ann. Reports*, 1926, 23, 139. See also K. J. P. Orton and A. E. Bradfield, *J.*, 1927, 896; *A.*, 655; A. E. Oxford and R. Robinson, *ibid.*, p. 2239; *A.*, 1065; R. C. Fawcett and R. Robinson, *ibid.*, p. 2414; *A.*, 1181; F. M. Irvine and J. C. Smith, *ibid.*, p. 74; *A.*, 240.

charge  $\delta +$  set up by (a) and (b) together operates against the movement of electrons towards the nucleus.



It might appear to follow from this explanation that the *m*-directive power of a benzoyl carbonyl group should be decreased by its attachment to an ethereal oxygen (as in  $\text{R}\cdot\text{O}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ ) or amino-nitrogen atom, for an exactly similar reason (II), namely, that the demand created by process (a) can be supplied, not only by (y) leading to *m*-substitution, but also by (b), which therefore opposes *m*-substitution. If this were so, a series of groups such as  $\text{CR}_3$ ,  $\text{NR}_2$ ,  $\text{OR}$ ,  $\text{Cl}$  should stand in the same order, as regards their power of competing with phenyl in supplying electrons to the carbonyl group, as they do in regard to their power of furnishing electrons by an identical mechanism to a directly attached benzene ring (in  $\text{C}_6\text{H}_5\cdot\text{CR}_3$ ,  $\text{C}_6\text{H}_5\cdot\text{NR}_2$ ) when *op*-substitution results. This order is known and is given by  $\text{N} > \text{O} > \text{Cl} > \text{C}$ , the group with the most active unshared valency electrons heading, and that with none terminating, the series. It follows that increasing *m*-directive power should be observed in the series

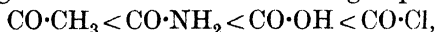


but this is opposed to the facts.

It has, however, been shown that a close analogy exists between the manner of *m*-orientation by the carbonyl group and that of *m*-orientation by nitroxyl, sulphonyl, and ammonium-salt groups, in which admittedly the influence of a dipole is under observation. Thus the *m*-directing action of the carbonyl group can be transmitted through an intervening saturated carbon atom which renders impossible (at least, on accepted theory) the mutually dependent displacements (y) (a) in (II). Such an effect is readily discernible in the nitration of ethyl phenylacetate (*meta*- 9%) and ethyl phenylmalonate (*meta*- 20%).<sup>15</sup> It is therefore concluded that in the carbonyl group there is a permanent separation of electrical charges in the sense to be expected from the view that the shared electrons of the double link will on the average be closer to the stronger atomic nucleus.<sup>16</sup> Similar considerations are applied to  $\text{C}\equiv\text{N}$  and  $\text{N}\equiv\text{O}$ , although here the disparity between the nuclei and hence the dissymmetry of the shared electrons, is less; and with limitations to  $\text{C}-\text{O}$ ,  $\text{C}-\text{F}$ , etc., in which the single-bond electrons are regarded as subject to smaller displacements.

<sup>15</sup> J. W. Baker and C. K. Ingold, *J.*, 1927, 832; *A.*, 558.    <sup>16</sup> *Idem*, *ibid.*

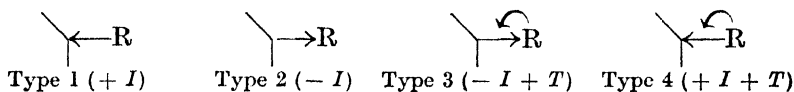
Returning to the consideration of the composite systems (I) and (II), it is evident that the conclusion represented by (I) remains, for the charge  $\delta +$  produced by (a) and (b) must always oppose *op*-substitution. On the other hand, (II) is seen to be fallacious, especially as regards (y). The preferable view is that each bond between carbon and oxygen represents a small dipole, the whole group being represented by  $\overset{\delta+}{\text{C}}\overset{\delta-}{\text{O}}$ , the positive field of which gives rise to *m*-orientation.<sup>17</sup> Processes (a) and (b) certainly must occur; but their effect (speaking approximately) is only to transfer electricity from one oxygen atom to the other, leaving unchanged both the total negative electrification on the two taken together and the total positive electrification on the carbon atom between them. It follows that the effect of the dipole  $\text{C}=\text{O}$  must *enhance* that of the dipole  $\text{C}=\text{O}$  in the group  $\text{CO}_2\text{R}$ . The enhancement by the corresponding single bond in  $\text{CO}\cdot\text{NH}_2$  would be less, and in  $\cdot\text{CO}\cdot\text{Cl}$  (by analogy with expectation in the case of  $\cdot\text{CO}\cdot\text{F}$ ) greater, thus accounting for the observed *m*-orienting sequence



in which the proportion of *m*-nitration rises as indicated by the figures 55, 69, 82, 90%.

*Transmission of Orienting Effects.*—The proportion of the isomerides formed in an oriented substitution is, of course, a mere ratio of velocities, and without supplementary data gives no information respecting the effect of the orienting group on the reactivity of the nuclear positions substituted. This matter is, however, of importance, both in connexion with the behaviour of the groups and also in relation to the various possible ways in which their effect may be transmitted throughout the aromatic nucleus.

In an attempt<sup>18</sup> to elucidate the broader features of the situation orienting groups have been divided into four categories represented by the following combinations of inductively propagated electronic strain (*I*,  $\curvearrowright$ ) and tautomeric (electromeric) transformations, (*T*,  $\longrightarrow$ ):



Type I includes the *op*-substituting saturated hydrocarbons, of which toluene is the simplest example. Type 2 is exemplified by phenylammonium and benzenesulphonyl compounds; and on account of the considerations mentioned above, benzoyl compounds also are included in this class, which thus embraces all known

<sup>17</sup> K. E. Cooper and C. K. Ingold, *J.*, 1927, 836; *A.*, 558.

<sup>18</sup> C. K. Ingold and F. R. Shaw, *ibid.*, p. 2918.



*m*-substituting benzene derivatives. In type 3 the influence of additional electrons which can be shared with the ring is superimposed on the circumstances of type 2, as in phenylthionium compounds, phenyl sulphoxides, phenyl halides, anisole, etc. In type 4 the effect of unshared electrons is added to the circumstances of type 1, as in the phenoxide ion.

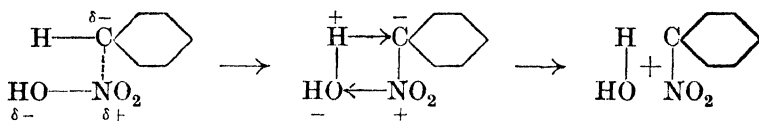
Type 1 is illustrated by toluene. Since the data representing the recognised *op*-orienting power of the methyl group are essentially ratios, they may have arisen in various ways. For instance, the methyl group may have caused an increased *op*-reactivity and a decreased *m*-reactivity; or it may have produced an increased *op*-reactivity and left the *m*-positions unaffected; or, again, it may have caused a large increase in *op*-reactivity and a smaller increase in *m*-reactivity. Actually the last alternative is the correct one, for a combination of velocity and orientation data for nitration shows that the methyl group increases the reactivity (as measured by reaction velocity) of each *o*-position 27·6-fold, that of the *p*-position 34·6-fold, and that of each *m*-position 2·1-fold. In type 2 exactly the reverse occurs: the reactivity of the *o*- and *p*-positions is decreased greatly and that of the *m*-positions to a smaller extent. Thus in Case 1, *m*-substitution arises from second-order *m*-activation, and in Case 2 from second-order *m*-de-activation, and it is concluded that inductive effects reach the *op*-positions in the first instance, but that a second-order effect, necessarily of the same sign as the primary effect, is relayed on to the *m*-position.

Case 3 is complex, and a series can be constructed such as  $\text{NRR}'$ , OR, I, Br, Cl, F representing progressively increasing  $-I$  and diminishing  $+T$ . All the groups mentioned are *op*-orienting, but throughout the series nuclear reactivity diminishes; and the coefficients representing it become fractional at a point between iodine and bromine. From this point to the left in the series,  $+T$  dominates  $-I$  in so far as the *op*-positions are affected; yet there is no *m*-substitution. It is concluded that, unlike  $-I$ , the effect  $+T$  cannot undergo a similar degree of relay to the *m*-position, and hence that there is a fundamental difference in the mode of transmission of  $I$  and  $T$  in the nucleus. Type 4 is straightforward and elucidates no new principle. The suggestion made is that the difference between the modes of transmission of  $I$  and  $T$  is a difference both of path and of mechanism, so that whereas  $I$  represents a permanent molecular condition,  $T$  (as the terminology implies) is an essentially temporary phenomenon which arises at the "call" of the reagent. It is consistent with knowledge of reactivity transmission in general that the *op*-charges produced by the inductive effect should be partly transmitted to the *m*-carbon

atom; on the other hand, it is difficult to see how the *op*-charges which would be produced by tautomeric electron displacements can avoid a similar degree of transmission, unless it be that these displacements become large only at those moments when the reagent molecule which excites them is already committed to ortho- or para-attack.

The effect of nuclear deactivation by a *m*-orienting group in causing substitution in another nucleus in polynuclear compounds was referred to in last year's Report (p. 134), and this year additional examples in the naphthalene and quinoline series have become available.<sup>19</sup>

*The Attack of Reagent Molecules.*—So far as concerns the constitution of the reagent, two factors would be expected to contribute to the effectiveness of its attack. The first is its polarisability, which determines the affinity of the molecule as a whole for the activated positions in the aromatic nucleus; the second is the affinity of the eliminated portion for hydrogen as measured inversely by the tendency to electrolytic dissociation of the simple molecule formed. The essential collaboration of the two factors has been pictured by means of the following illustrative scheme :<sup>20</sup>



The influence of the first factor is well illustrated by reference to halogenation.<sup>21</sup> It requires that the activity of a chlorinating agent  $X\cdot Cl$  should increase with the electron affinity of  $X$ , and similarly for bromination and iodination; and this agrees with the fact that bromine monochloride is a powerful brominating agent but does not chlorinate, that similarly iodine monochloride iodates, and that generally the efficiency of the more commonly employed halogenating agents is in the anticipated order (electron-affinity sequence :  $Cl > Br > I > OH$ ) :



On the other hand, hypoiodous acid is irregular : it is a *more* powerful iodinating agent than is iodine ; and this, as F. G. Soper

<sup>19</sup> B. H. Ingham, *J.*, 1927, 1972; **A.**, 963; E. Roberts and E. E. Turner *ibid.*, p. 1832; **A.**, 975.

<sup>20</sup> *Ann. Reports*, 1926, **23**, 135.

<sup>21</sup> C. K. Ingold, E. W. Smith, and C. C. N. Vass, *J.*, 1927, 1245; **A.**, 762.

and G. F. Smith observe,<sup>22</sup> probably means that the second of the factors mentioned cannot be neglected. Iodine and hydroxyl are neighbouring members of the above series, and it may well be that the difference of their electron affinities is outweighed by the disparity between the strong tendency of hydrogen and hydroxide ions to form undissociated water and the relatively slight tendency of hydrogen and iodide ions to yield readily ionising hydrogen iodide.

Further instances have been given of the substitution of halogens by hydrogen in *op*-halogenated amines and phenols,<sup>23</sup> but the subject is not yet in a suitable state for summarisation.

*Migrations from Side Chain to Nucleus.*—The researches on this subject which were reported to the British Association between 1907 and 1915 are now classical, and Orton's demonstration that the "rearrangement" of *N*-chloro-*N*-acylarylamines in the presence of hydrochloric acid is an intermolecular process depending on the intermediate production of chlorine has occasionally led to the assumption that the apparently similar migrations of groups other than chlorine depend on a corresponding mechanism—despite the statement<sup>24</sup> that preliminary experiments with nitroamines had indicated that the re-arrangements of these substances appeared very difficult to interpret in this way.

The remarkable fact appears to be that these reactions (*e.g.*, migration of X in Ar·NRX when X = Cl, OH, NO<sub>2</sub>, Alk, NHAr, N<sub>2</sub>Ar), although formally so similar, are divisible into two categories.<sup>21</sup> Thus the re-arrangements of diazoamino-compounds (X = N<sub>2</sub>Ar) almost certainly proceed by the intermolecular mechanism, the last stage being a diazo-coupling. On the other hand, not only the re-arrangement of nitroamines, but also that of arylhydroxylamines, and of diarylhydrazines (semidine and benzidine changes), appear to be essentially intramolecular processes. It is true that the evidence for this is mainly of a negative kind, but it would seem that the tests for an intermolecular process which have been applied to these reactions ought certainly to have detected it.

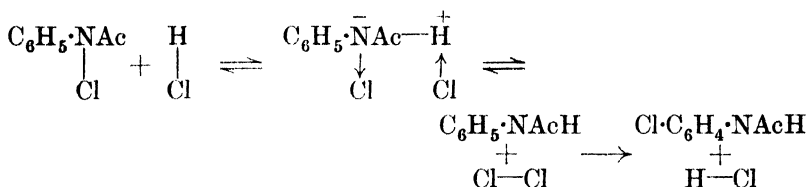
The intermolecular processes are the less difficult to understand. In the case of *N*-chloroacetanilide, for instance, a hydrion may be assumed to co-ordinate with the nitrogen atom through its lone electrons, producing a charge which leads to the ejection of positive

<sup>22</sup> *J.*, 1927, 2757.

<sup>23</sup> B. H. Nicolet and J. R. Sampey, *J. Amer. Chem. Soc.*, 1927, **49**, 1796; **A.**, 868; B. H. Nicolet and W. L. Ray, *ibid.*, p. 1801; **A.**, 869; B. H. Nicolet and R. B. Sandin, *ibid.*, p. 1806; **A.**, 868.

<sup>24</sup> *Brit. Assoc. Reports*, 1912, 117.

chlorine in combination with a chloride ion; the chlorine molecule thus formed then chlorinates a molecule of acetanilide. This is essentially Orton's theory of the process:



The intramolecular changes are more difficult to visualise, and appear to require the assumption of an internal path to the *p*-position.

A characteristic of the intermolecular kind of "migration" is that it must obey ordinary orientation laws and need not necessarily follow the *op*-migration rule. The migrations of aryl iodide dichlorides belong to the intermolecular type, and therefore the chlorine in the dichloride of *o*-iodoanisole does not go into the position para to the iodine atom, as is stated in the literature, but into the meta-position, because this is para to the methoxy-group, which is the stronger directing agent.<sup>25</sup>

*Side-chain Reactivity.*—S. C. J. Olivier has proved <sup>26</sup> that a close "correspondence" exists between the factors controlling nuclear reactivity in benzene derivatives and those which govern certain side-chain reactions in derivatives of toluene. The most elementary view which could be taken of these side-chain reactions might be expressed by stating that a nuclear substituent which increases the nuclear reactivity in a given position (*i.e.*, supplies electrons) should also facilitate a reaction in a side chain attached to that position if the reaction depends, in regard to its speed, on the separation of a negative ion or the addition of a positive one; and conversely should inhibit a side-chain reaction if this depends on the addition of a negative ion or the separation of a positive one. A nuclear substituent which depresses nuclear reactivity (withdraws electrons) should act in the opposite way. There is evidence that this simple view is not entirely adequate; nevertheless it forms a convenient starting point for the consideration of some data which have recently been presented.

Olivier's principle of correspondence is largely based on a study of the rates of hydrolysis of substituted benzyl chlorides in aqueous

<sup>25</sup> C. K. Ingold, E. W. Smith, and C. C. N. Vass, *loc. cit.* Compare S. A. Brazier and H. McCombie, *J.*, 1912, **101**, 968.

<sup>26</sup> *Rec. trav. chim.*, 1923, **42**, 775; *A.*, 1923, i, 908; S. C. J. Olivier and G. Berger, *ibid.*, 1927, **46**, 605; *A.*, 1177.

alcohol, and is illustrated by the following coefficients, referred to that of benzyl chloride as unity (temp. 83°) :

Substituent.	Velocity.	Substituent.	Velocity.	Substituent.	Velocity.
$p\text{-CH}_3$	10.6	$p\text{-Br}$	0.50	$m\text{-CO}_2\text{H}$	0.245
$o\text{-},,$	4.84	$o\text{-},,$	0.286	$p\text{-},,$	0.165
$m\text{-},,$	1.39	$m\text{-},,$	0.215	$m\text{-NO}_2$	0.090
$p\text{-Cl}$	0.62	$p\text{-I}$	0.477	$o\text{-},,$	0.084
$o\text{-},,$	0.355	$o\text{-},,$	0.287	$p\text{-},,$	0.074
$m\text{-},,$	0.237	$m\text{-},,$	0.201		

Thus for  $\text{CH}_3$ , Cl, Br, I the relation is  $o,p,>m$ , and these are *op*-orienting groups in the ordinary sense; for  $\text{CO}_2\text{H}$  and  $\text{NO}_2$  the relation is  $m>o,p$ , and these groups are *m*-orienting. That is to say, those isomerides in which  $-\text{CH}_2\text{Cl}$  is attached to the nuclear carbon atom which is preferentially attacked during substitution of the corresponding benzene derivative are the ones which are most readily hydrolysed; <sup>27</sup> or, as Olivier more broadly expresses it, the "lability of the atoms *Cl* and *H* in the molecules  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CH}_2\text{Cl} \\ \text{X} \end{smallmatrix}$  and  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{H} \\ \text{X} \end{smallmatrix}$  is influenced analogously by the substituent X" (in the reactions considered).

A further subdivision is possible amongst the *op*-orienting groups, for  $\text{CH}_3$  in any position increases the rate of hydrolysis, whereas the three halogens decrease it. This partly corresponds to the circumstance (above) that methyl increases the speed of nuclear substitution in all positions, whereas the halogens chlorine and bromine decrease it; but it will be observed that the comparison fails with iodine, and that this irregularity is part of the wider anomaly that the three halogens <sup>28</sup> are in the reverse of the anticipated order amongst themselves, indicating the operation of some other principle, possibly connected with the circumstances mentioned on p. 152. It is consistent that the *m*-orienting groups decrease the rate of hydrolysis.

In these experiments the medium was acidic, and for this, as well as for structural reasons, it need not be assumed that the addition of hydroxide ions constitutes the first stage of the hydrolysis. The alternative is that the separation of a chloride ion is the first stage, and as this must be the slow stage (since intermediate products are not present in appreciable concentration), it follows that the correspondence between the lability of Olivier's "*Cl*" and "*H*" should be (as it is) in the direct and not in the inverse sense. Similar conditions obtain for the condensation of substituted benzyl chloride with benzene in the presence of alumin-

<sup>27</sup> J. B. Shoosmith and W. E. Taylor, *J.*, 1926, 2832; *A.*, 1927, 50.

<sup>28</sup> J. B. Shoosmith and R. H. Slater's experiments (*J.*, 1926, 214; *A.*, 1926, 389) indicate that fluorine falls into line with the other halogens in this respect.

ium chloride, which likewise shows correspondence in the direct sense.<sup>29</sup> On the other hand, A. Tasman's experiments on the velocity of opening of the phthalide ring are of interest as exhibiting precisely the opposite phenomena.<sup>30</sup> These reactions were carried out in alkaline<sup>31</sup> solution, and every analogy (of which the most cogent is Lapworth's demonstration of the mechanism of cyanohydrin formation) points to the conclusion that the initial stage (again, the rate-determining stage) consists in the addition of hydroxide ions at the carbon end of the carbonyl double linking. Therefore, theoretically, the situation is exactly the reverse of that which obtains in the acid hydrolysis of benzyl halides. The velocities (referred to that for phthalide as unity) are in the bottom line of the following table, and the substituents indicated were all in the 5-position, that is, the meta-position to the carbonyl group :

<i>m</i> -Substituent	NH <sub>2</sub>	NHAc	Me	H	Cl	Br	I	CN	NO <sub>2</sub>
Rate (Olivier)	—	—	1.39	1.00	0.24	0.22	0.20	—	0.09
Rate (Tasman)	0.31	0.75	—	1.00	1.32	1.53	2.00	5.71	10.6

Olivier's results for *m*-substituted benzyl chlorides are given for comparison. It will be obvious that those substituents which retard the acid hydrolysis of a benzyl chloride accelerate the alkaline hydrolysis of a phthalide, and that the substituents investigated for the two cases stand in the inverse order with regard to their effect; that is to say, Olivier's "correspondence" becomes an inverse correspondence in the example studied by Tasman. Again, the anomalous order of the three halogens is noticed, indicating that the effect referred to above is real.

In the hydrolysis of benzoyl chlorides more complicated conditions are revealed. For example, in the series of substituents CH<sub>3</sub>, Cl, Br, NO<sub>2</sub>, instead of finding a regular increase or decrease in the speed of hydrolysis, G. Berger and S. C. J. Olivier<sup>32</sup> observed

<sup>29</sup> S. C. J. Olivier and G. Berger, *Rec. trav. chim.*, 1926, **45**, 710; 1927, **46**, 605; **A.**, 1926, 1139; 1927, 1177.

<sup>30</sup> *Ibid.*, 1927, **46**, 653; **A.**, 1186.

<sup>31</sup> It is important to recognise the effect of experimental conditions. For example, the regularities observed by Olivier in connexion with the rates of hydrolysis of benzyl chlorides disappear (tend to become inverted) when a new mechanism is allowed to enter by the use of alkaline solutions (H. Franzen and I. Rosenberg, *J. pr. Chem.*, 1920, [ii], **101**, 333; **A.**, 1921, i, 233). J. B. Shoesmith and R. J. Connor record (*J.*, 1927, 1769; **A.**, 962) that a nuclear methyl group depresses the speed of hydrolysis of  $\beta$ -phenylethyl bromides, "the reverse of the case in the corresponding benzyl bromides." The validity of this comparison and the implied indication of an alternating effect is challengeable, however, because, amongst other reasons, the  $\beta$ -phenylethyl compounds were hydrolysed in *alkaline* solutions, whereas acid media had previously been employed (J. B. Shoesmith and R. H. Slater, *J.*, 1924, **125**, 2278; **A.**, 1925, i, 16) for the hydrolysis of the benzyl compounds.

<sup>32</sup> *Ibid.*, 1927, **46**, 516; **A.**, 835.

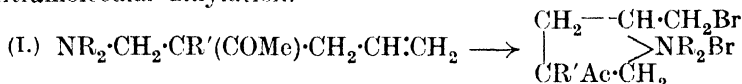
a minimum: the highest velocities were obtained with  $\text{CH}_3$  and  $\text{NO}_2$  as substituents (with *o*-methyl the speed was too great to be measured), whereas Cl and Br gave velocities between 0.8 and 1.7 times that of unsubstituted benzoyl chloride. It appears that some such effect might have been expected from the foregoing analysis; for in  $\text{COCl}$  both the additive power of the carbonyl group and the tendency to ionisation of the halogen might contribute to the observed result, so that a nuclear substituent which inhibits one mechanism would accelerate the other; in either case it will be the acceleration which becomes obvious experimentally.

C. K. INGOLD.

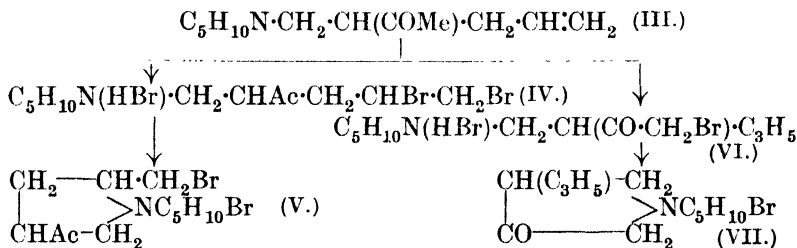
### PART III.—HETEROCYCLIC DIVISION.

#### *Pyrroles.*

APART from a considerable number of papers on blood, bile, and other pigments and their decomposition products, comparatively little work has been published on pyrroles during the year. C. Mannich and T. Gollasch<sup>1</sup> have described the preparation of pyrrolidines from ketoalkylamines (I) by converting them into dibromides, which readily pass into the corresponding pyrrolidines by a kind of intramolecular alkylation.



In some cases, different products are formed from the same substance, depending on the conditions of the experiment; thus in the following scheme, changes (III) to (V) are induced by adding bromine to the hydrobromide of the primary material (III) and changes (III)  $\longrightarrow$  (VI)  $\longrightarrow$  (VII) by addition of bromine to the primary base (III) itself. ( $\text{C}_5\text{H}_{10}\text{N}$  = piperidyl)



A. Müller and A. Sauerwald<sup>2</sup> have applied W. Marckwald and A. von Droste-Huelshoff's method of preparing secondary amines<sup>3</sup>

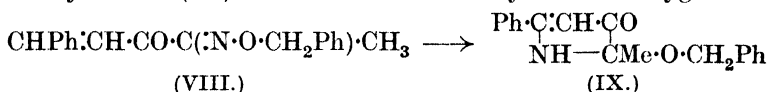
<sup>1</sup> *Annalen*, 1927, **453**, 177; *A.*, 572.

<sup>2</sup> *Monatsh.*, 1927, **48**, 155; *A.*, 884.

<sup>3</sup> *Ber.*, 1898, **31**, 3261; *A.*, 1899, i 289.

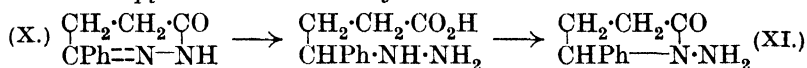
to  $\alpha\delta$ -dibromobutane and find that when this is condensed with *p*-toluenesulphonamide in presence of potassium hydroxide solution, a good yield of *N-p*-toluenesulphonylpyrrolidine is produced, from which pyrrolidine is not obtainable except by hydrolysis with hydrochloric acid in closed vessels at 160°.

Whereas most oximes and phenylhydrazones are converted by perchloric acid into perchlorates, which are dissociated by water, the perchlorate of the benzyl ether of  $\alpha$ -phenyl- $\Delta^{\alpha}$ -pentene- $\gamma$ - $\delta$ -dione- $\delta$ -oxime (VIII), on treatment with water, undergoes a kind of Beckmann transformation to 3-keto-5-phenyl-2-methylpyrroline 2-benzyl ether (IX). This substance readily absorbs oxygen from

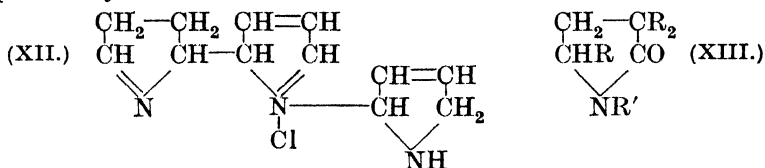


the air and when the analogous 2-phenylmethylamino-3-keto-5-phenyl-2-methylpyrroline, prepared from the corresponding phenylmethylhydrazone, is shaken with oxygen a well-defined dioxide is produced.<sup>4</sup>

In an attempt to prepare  $\gamma$ -hydrazinic acids by the reduction of the hydrazones of  $\gamma$ -ketonic acids, A. Darapsky<sup>5</sup> converted  $\beta$ -benzoylpropionic acid into 3-phenylpyridazinone<sup>6</sup> (X), but this on reduction with sodium amalgam gave, instead of the expected acid, 1-amino-5-phenyl-2-pyrrolidone (XI), probably by anhydride formation from  $\gamma$ -hydrazino- $\gamma$ -phenylbutyric acid, produced intermediately in the reduction:  $\alpha$ -ketoglutaric acid behaves similarly, giving 1-amino-2-pyrrolidone-5-carboxylic acid.



B. V. Tronov and P. P. Popov <sup>7</sup> suggest that tripyrrole, produced by polymerisation of pyrrole with hydrochloric acid, has the formula (XII), since the substance obtained from it by treatment with alkali contains oxygen and is presumably the hydroxide of a quaternary base. Such formulæ also account for a number of



other anomalous points in the behaviour of polymerised pyrroles.

\* O. Diels, O. Buddenberg, and S. Wang, *Annalen*, 1927, **451**, 223; **A.**, 253.

<sup>5</sup> [With J. van der Beck and E. Philipp] *J. pr. Chem.*, 1927, [ii], **116**, 129; **A.**, 672.

\* Compare S. Gabriel and J. Colman, *Ber.*, 1899, **32**, 399; *A.*, 1899, i, 390.

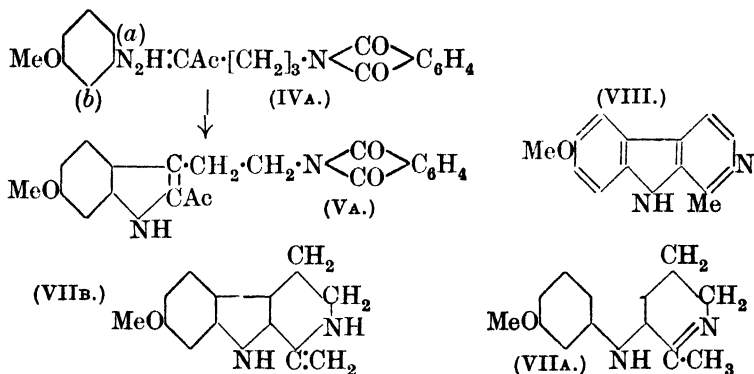
<sup>7</sup> *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 745; **A.**, 1927, 775.





yielding insoluble phthalylhydrazide (VI) and a solution from which harmalan (VII) could be extracted. The latter on oxidation with chromic acid yields harman (demethoxyharmine), identical with that obtainable from harmine.

When in the above series of reactions benzenediazonium chloride is replaced by *m*-methoxybenzenediazonium chloride, the product at stage (IV) is represented by (IV<sub>A</sub>). In this material, ring closure might occur at (a) or (b), producing, owing to the methoxyl group, different substances. This point has already been investigated for a strictly analogous product, which leaves no doubt that (a) is the favoured position.<sup>10</sup> Ring closure was effected by the use of *n*-butyl-alcoholic hydrogen chloride to 6-methoxy-2-acetyl-3-β-phthalimidoethylindole (V<sub>A</sub>), which with hydrazine hydrate gave harmaline (VII<sub>A</sub>) identical with the natural base and, like it, oxidisable to harmine.

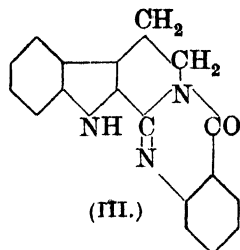
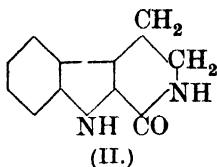
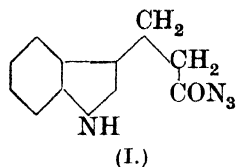


Of the other two possible formulæ for harmaline, *viz.*, (VII<sub>B</sub>) and that in which the chain  $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CMe}-$  is replaced by  $-\text{CH} \cdot \text{CH} \cdot \text{NH} \cdot \text{CHMe}-$ , only (VII<sub>B</sub>) is consistent with this synthesis. It has been shown already that methylharmaline and acetylharmaline<sup>11</sup> are derivatives of this tautomeric form, but most of the reactions of the substance are in harmony with the view that this configuration is assumed with difficulty.

**Rutaecarpine.**—Closely connected with the work on harmaline just described is the synthesis of rutaecarpine. In an attempt to apply the Curtius reaction to β-3-indolylpropionic acid for the preparation of 3-β-aminoethylindole, the acid was converted into the azide (I).

<sup>10</sup> W. O. Kermack, W. H. Perkin, jun., and R. Robinson, *J.*, 1921, 119, 1614.

<sup>11</sup> H. Nishikawa, W. H. Perkin, jun., and R. Robinson, *J.*, 1924, 125, 657; *Ann. Reports*, 1924, 21, 141.



This in benzene solution in presence of hydrogen chloride is converted into 3-keto-3:4:5:6-tetrahydro-4-carboline<sup>12</sup> (II). The latter condenses with methyl anthranilate in presence of phosphorus trichloride<sup>13</sup> to form rutaecarpine<sup>14</sup> (III).

### Pyridine Derivatives.

Although much interesting work has been published on pyridine compounds, most of it is the result of further exploration of reactions which have been referred to previously in these reports and presents few features of general interest.

C. Mannich and K. Curtaz<sup>15</sup> have further investigated the synthesis of ketonic bases by the interaction of formaldehyde, ketonic acids, and amines. The reaction appears to be quite general for substituted  $\beta$ -ketonic acids and secondary amines, but with ammonia or primary amines it is complicated and well-defined products have not yet been isolated. In unsubstituted  $\beta$ -ketonic acids, both hydrogen atoms of the reactive methylene group may be replaced; thus acetoacetic acid gives a mixture of the mono- and di-amine,  $\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NR}'\text{R}''$  and  $\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{NR}'\text{R}'')_2$ . The present paper deals principally with piperidine as the secondary amine: it gives, for example, with ethyl benzylacetoacetate and formaldehyde,  $\delta$ -phenyl- $\gamma$ -piperidinomethylbutan- $\beta$ -one,  $\text{Me}\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\cdot\text{NC}_5\text{H}_{10})\cdot\text{CH}_2\text{Ph}$ , which on reduction furnishes the corresponding alcohol, the benzoyl derivative of which possesses local anæsthetic properties.

C. Dufraisse and H. Moureu<sup>16</sup> find that the type of action shown by piperidine on  $\alpha$ -bromobenzylideneacetophenone investigated by E. R. Watson<sup>17</sup> occurs generally with  $\alpha$ -bromo- $\alpha$ -unsaturated ketones and may give rise either to an unsaturated monopiperidide,  $\text{COR}\cdot\text{C}(\text{NC}_5\text{H}_{10})\cdot\text{CHR}'$ , or to a dipiperidino-compound of the

<sup>12</sup> R. H. F. Manske and R. Robinson, *J.*, 1927, 240; **A.**, 256.

<sup>13</sup> Compare M. Sen and J. N. Rây, *J.*, 1926, 646; **A.**, 1926, 606.

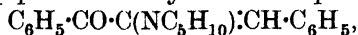
<sup>14</sup> Y. Asahina, R. H. F. Manske, and R. Robinson, *J.*, 1927, 1708; **A.**, 982.

<sup>15</sup> *Arch. Pharm.*, 1926, 264, 741; **A.**, 1927, 231; compare *Ber.*, 1924, 57, [B], 1108; **A.**, 1924, i, 847.

<sup>16</sup> *Bull. Soc. chim.*, 1927, [iv], 41, 457, 850; **A.**, 571, 884.

<sup>17</sup> *J.*, 1904, 85, 1322.

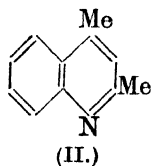
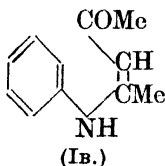
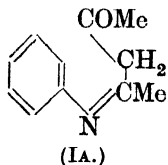
type  $\text{COR} \cdot \text{C}(\text{NC}_5\text{H}_{10})_2 \cdot \text{CH}_2\text{R}'$  or  $\text{COR} \cdot \text{CH}(\text{NC}_5\text{H}_{10}) \cdot \text{CHR}' \cdot \text{NC}_5\text{H}_{10}$ , depending on the nature of the original ketone. The monopiperidino-compounds are hydrolysed by dilute acid to the corresponding diketones, *e.g.*,  $\omega$ -piperidinobenzylideneacetophenone,



yields phenylbenzylglyoxal,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ . The dipiperidine derivatives behave similarly, furnishing the  $\alpha\beta$ -diketones and an aminoketone, in proportions depending on the nature of the original ketone: thus dipiperidinoethylacetophenone yields chiefly  $\omega$ -piperidinoacetophenone,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NC}_5\text{H}_{10}$ , and acetaldehyde with small amounts of propionylbenzoyl, indicating that it has the  $\alpha\beta$ -structure,  $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}(\text{NC}_5\text{H}_{10}) \cdot \text{CHMe} \cdot \text{NC}_5\text{H}_{10}$ .

#### Quinoline Group.

E. Roberts and E. E. Turner<sup>18</sup> find that in the first stage of the Combes synthesis<sup>19</sup> of 2:4-dimethylquinolines, *viz.*, condensation of primary aromatic amines with acetylacetone to form products of type (IA) or (IB), ease of condensation is conditioned mainly by the basicity of the substituted aniline used, and only to a slight extent by steric factors, since, although *o*-, *m*-, and *p*-chloro-, 2:4-, 3:4-, and 3:5-dichloro-anilines condense and 2:5-dichloroaniline does so partly, no nitroaniline derivative can be made to undergo this reaction. In the second stage, *viz.*, ring closure to a 2:4-dimethyl quinoline (II) by warming with sulphuric acid, the effect of the nature of the substituents in the benzene ring is much more apparent. Ring closure occurs readily if a strongly *o-p*-directive substituent is present in position 3 or 5 (IA) with respect to the nitrogen atom: thus of the three chloroanilines, only one, *m*-chloroaniline, can be so converted, and this yields 7-chloro-2:4-dimethylquinoline, the steric factor favouring the 7- instead of the 5-position.



Of the three dichloroanilines used (see above), only the 3:4-derivative could be converted by this method and this gave 6:7-dichloro-2:4-dimethylquinoline. The 3:5-compound, in spite of the fact that both chlorines are meta to the nitrogen atom, is not so convertible, owing, it is suggested, to inhibition by steric influence, although this is not exhibited in the case of the 2:5-, 3:4-

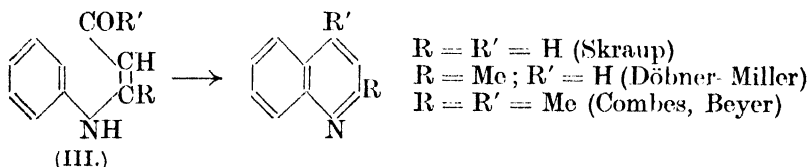
<sup>18</sup> *J.*, 1927, 1832; *A.*, 975.

<sup>19</sup> *Bull. Soc. chim.*, 1888, 49, 90; *A.*, 1888, 504.

2 : 3-dimethoxy- and the 2-bromo-4 : 5-dimethoxy-anilines, which all undergo ring closure.

The Beyer synthesis<sup>20</sup> from amine, paraldehyde, and acetone also is subject to steric influence, but apparently much less so, since by this method quinolines can be prepared from *o*-, *m*-, and *p*-chloro- and from 2 : 4-, 2 : 5-, 3 : 4-, and 3 : 5-dichloro- as well as from 2 : 4 : 5-trichloro-anilines, although the yields are poor.

In the Skraup and the Döbner-Miller syntheses the steric factor is much less effective and in general *m*-directive substituents in the *m*-position in aniline give 5-substituted quinolines, whereas *o*-*p*-directive substituents in the same position yield 5- or 7-substituted quinolines or both. In all four methods of synthesis the final product in which ring closure occurs can be regarded as represented by type formula (III) and possibly the essential difference



in the condensations feasible by the first and second pairs of methods is due to the fact that in the second pair (Combes, Beyer) R' is a methyl group, whereas in the first pair R' is a hydrogen atom : thus in the Skraup reaction *m*-chloroaniline gives a mixture of 5- and 7-chloro-derivatives; in the Beyer reaction, mainly the 7-derivative; and in the Combes synthesis, only 7-chloro-2 : 4-dimethylquinoline.

The principal factor governing nitration of the 2 : 4-dimethylquinolines is the reactivity of the hydrogen atoms in the 5- and 8-positions, and also the *o*-*p*-directive influence of chlorine in the case of their chloro-derivatives. The nitrogen of the pyridine ring appears to exert no influence. Allowance being made for the known low reactivity of the pyridine ring, the reactivity of hydrogen in the 5- and 8-positions is to be expected, since they alone correspond to the  $\alpha$ -positions in naphthalene.<sup>21</sup>

Sven Bodforss<sup>22</sup> has published an interesting paper on the by-products of the Döbner-Miller synthesis, in which an attempt is made to elucidate the precise course of the reaction by studying the possible reactions of the components taken two at a time.

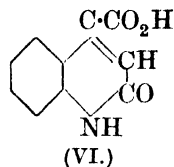
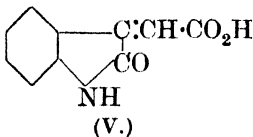
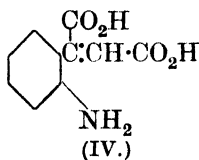
Theoretically two lactams are derivable from  $\beta$ -carboxy-*o*-amino-

<sup>20</sup> *J. pr. Chem.*, 1886, [ii], **33**, 393; *A.*, 1886, 629; compare J. H. Reed, *ibid.*, 1885, [ii], **32**, 630; *A.*, 1886, 370.

<sup>21</sup> Compare W. H. Mills and J. L. B. Smith, *J.*, 1922, **121**, 2724.

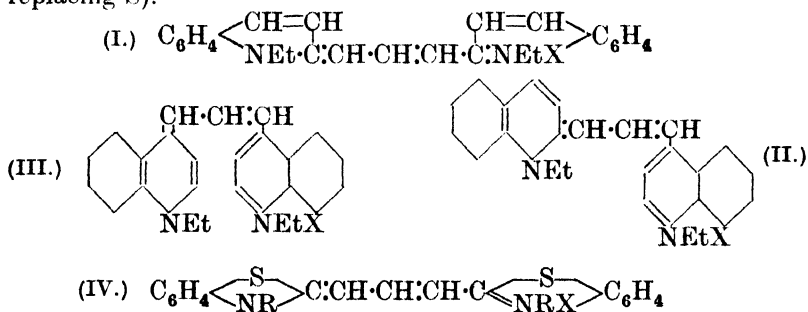
<sup>22</sup> *Annalen*, 1927, **455**, 41; *A.*, 775.

cinnamic acid (IV) and when ring closure takes place by acidification of alkaline solutions of the acid, the indolinone (V) or the 2-quinolone-4-carboxylic acid (VI) will be produced according to which is the more stable.



This acid (VI) has been repeatedly made by methods which in some cases indicate (V) as its probable structure,<sup>23</sup> but that it is correctly represented by (VI) is shown by the fact that it can be methylated to 1-methyl-2-quinolone-4-carboxylic acid, the ethyl ester of which is identical with that prepared by Thielepape<sup>24</sup> by a method which leaves no doubt that it is ethyl 1-methylquinolone-4-carboxylate. The dihydro-acid produced by hydrogenation of (VI) is identical with Grünacher and Mahal's<sup>25</sup> "oxindole-3-acetic acid." These results indicate generally that the quinolone is more stable than the indolinone ring.<sup>26</sup>

So far six species of carbocyanine dyes are known, the carbocyanines proper, in which the linking of the two 1-ethylquinoline nuclei takes place through the 2 : 2'- (I), 2 : 4'- (II), and 4 : 4'- (III) positions, the thiocarbocyanines (IV), the oxacarbocyanines (IV, with O replacing S), and the indocarbocyanines (IV, with CMe<sub>2</sub> replacing S).



The necessary condensations have been effected in various solvents and pyridine has been used for the thiocarbocyanines.<sup>27</sup> Miss F. M.

<sup>23</sup> See, for example, Borsche and Jacobs, *Ber.*, 1914, **47**, 354; *A.*, 1914, i, 322.

<sup>24</sup> *Ber.*, 1922, **55**, [B], 127; *A.*, 1922, i, 271.

<sup>25</sup> *Helv. Chim. Acta*, 1923, **6**, 467; *A.*, 1923, i, 713.

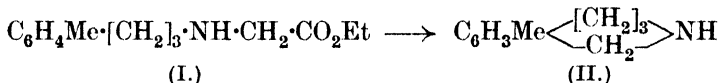
<sup>26</sup> J. A. Aeschlimann, *J.*, 1926, 2902; *A.*, 1927, 256.

<sup>27</sup> W. H. Mills, *J.*, 1922, **121**, 455; W. König and W. Meier, *J. pr. Chem.*, 1925, [ii], **109**, 324; *A.*, 1925, i, 706.

Hamer<sup>28</sup> has now found that all six classes can be produced in better yields by the use of boiling pyridine as a solvent and the method has already been applied in the preparation of new representatives of all six groups.

*isoQuinoline Group.*

The method of J. von Braun<sup>29</sup> for the preparation of cyclic imines has been further explored and shown to be applicable to glycines of the general formula  $C_6H_5 \cdot [CH_2]_n \cdot NR \cdot CH_2 \cdot CO_2H$ , where  $n = 2$  or  $3$ . The effect of successive, or sometimes simultaneous, use of phosphorus pentachloride and aluminium chloride is to convert the glycine into the acid chloride, which in presence of aluminium chloride loses carbon monoxide, ring closure then taking place, with the production, in the cases now considered, of tetrahydroisoquinolines or their ring homologues, *e.g.*, 8-methyl-*as*-homotetrahydroisoquinoline (II).

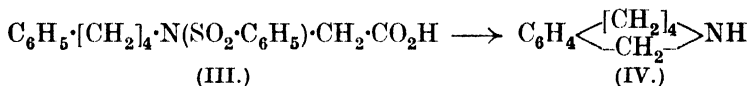


The method failed with homopiperonylglycine, which when used as the benzenesulphonyl derivative,

$CH_2O_2 \cdot C_6H_5 \cdot [CH_2]_2 \cdot N(SO_2 \cdot C_6H_5) \cdot CH_2 \cdot CO_2H$ ,

carbonised and yielded no dicyclic product.<sup>30</sup>

In the monocyclic series, ring closure has not so far been effected by these methods to produce a heterocyclic ring of more than seven members, but in the dicyclic series an eighth member has been introduced;<sup>31</sup> thus benzenesulphonyl- $\delta$ -phenyl-*n*-butylaminoacetic acid (III) yields a mixture of  $\delta$ -phenyl-*n*-butylamine and 7:8-benzoheptamethyleneimine (IV), but the next higher homologue,



benzenesulphonyl- $\epsilon$ -phenyl-*n*-amylaminoacetic acid, although it evolves carbon monoxide on treatment with phosphorus pentachloride and aluminium chloride, yields a product which on hydrolysis furnishes only  $\epsilon$ -phenyl-*n*-amylamine and complex substances.

In certain of these reactions the final operation is effected much more readily by the use of phosphoric oxide than by successive application of phosphorus pentachloride and aluminium chloride.

A number of interesting papers have been published, which are

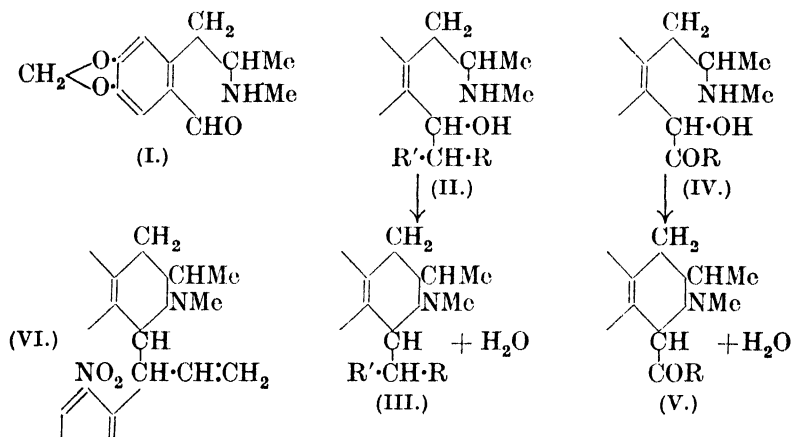
<sup>28</sup> *J.*, 1927, 2796.

<sup>29</sup> *Ann. Reports*, 1924, **21**, 132.

<sup>30</sup> J. von Braun and K. Wirz, *Ber.*, 1927, **60**, [B], 102; **A.**, 254.

<sup>31</sup> J. von Braun and O. Bayer, *ibid.*, p. 1257; **A.**, 673.

of importance in connexion with work on complex natural products derived from *isoquinoline*. Among these may be mentioned the synthesis of 8-nitro-5:6-dimethoxy-2-methyl-1:2:3:4-tetrahydro*isoquinoline* by R. D. Haworth,<sup>32</sup> and the observation that the nitro-group in this position does not enhance the reactivity of the 1-methylene group. M. Oberlin<sup>33</sup> has shown that methylhydrastinine (I) condenses more easily than hydrastinine with substances containing mobile hydrogen, to form derivatives of 1-hydromethylhydrastinine,<sup>34</sup> *e.g.*, with acetone, ethyl phenylacetate and ethyl 2:4-dinitrophenylacetate, and, in presence of condensing agents, with numerous other substances such as *o*-nitrotoluene, aromatic aldehydes, etc. It is suggested that the condensation may be either of the aldol (II) or the benzoin (IV) type, according to the character of the reacting product, both forms eventually becoming dehydrated



to (III) and (V). The condensates with *o*-nitrotoluene are probably represented by (III) and those with *o*-nitroaldehydes by (V), since these are easily split by phenylhydrazine, giving phenylhydrazones.

A special type of condensation is that of *o*-nitrosafrole with methylhydrastinine. The ethylenic linking in the final product (VI) can be detected by hydrogenation, but not by bromination or by permanganate. Of indirect interest also are new syntheses of hydrastic acid<sup>35</sup> and safrole,<sup>36</sup> the latter being obtainable by the methylenation of 1:2-dihydroxy-4-allylbenzene with methylene

<sup>32</sup> *J.*, 1927, 2281; *A.*, 1085.

<sup>33</sup> *Arch. Pharm.*, 1927, 265, 274; *A.*, 681.

<sup>34</sup> Compare E. Hope and R. Robinson, *J.*, 1911, 99, 2114, and *Ann. Reports*, 1925, 22, 152; 1926, 23, 171.

<sup>35</sup> T. S. Stevens and Miss M. C. Robertson, *J.*, 1927, 2790.

<sup>36</sup> W. H. Perkin, jun., and V. M. Trikojus, *J.*, 1927, 1663; *A.*, 871.



iodide in acetone in presence of potassium carbonate, conditions which in this case ensure absence of tarry by-products.

**1-Benzylisoquinolines.**—A number of syntheses of papaverine<sup>37</sup> and allied substances have been effected, mostly by modifications of well-known methods. E. Späth and A. Burger<sup>38</sup> find that a 70% yield of laudanotine can be obtained in A. Pictet's synthesis if the final stage is effected by electrolytic reduction at a lead cathode of a solution of crude papaverine methosulphate in dilute sulphuric acid. The resulting *dl*-base can be partly hydrolysed (loss of MeO) to *dl*-laudanine by heating in sealed tubes with hydrochloric acid (*d* 1.19). *d*- and *l*-Laudanine can be converted in similar fashion into *d*- and *l*-laudanine, respectively, the latter being identical with the natural alkaloid laudanidine, thus finally establishing the relationships of these various alkaloids as described already.<sup>39</sup>

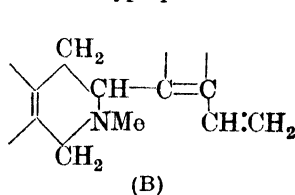
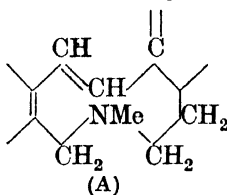
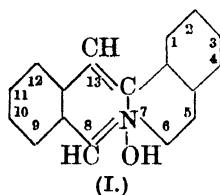
**Disoquinoline Alkaloids.**—A considerable amount of work has been done on this group of alkaloids during the year, chiefly in applying reactions that have now become almost standardised, to filling up lacunæ in knowledge of the group. The prototype of the series is protoberberine (I). The natural alkaloids immediately derivable from this are as follows :

Berberine :

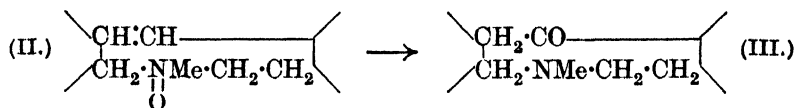
9 : 10-dimethoxy-2 : 3-methylenedioxy-derivative  $\rightarrow$   $\beta$ -homochelidonine.

Coptisine : 2 : 3 : 9 : 10-bismethylenedioxy-derivative  $\rightarrow$  protopine.

Palmitine : 2 : 3 : 9 : 10-tetramethoxy-derivative  $\rightarrow$  cryptopalmitine.



Each of these on reduction furnishes a tetrahydro-derivative, the methohydroxide of which on heating is capable of giving two anhydro-bases, as shown in partial formulæ A and B, representing the changes in the two inner rings. Anhydro-bases of the A type on oxidation by perbenzoic acid add one atom of oxygen to the methylimino-group, giving amine oxides (II) which are readily



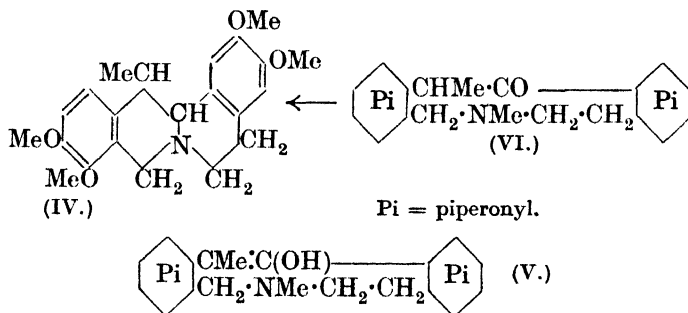
<sup>37</sup> K. W. Rosenmund, M. Nothnagel, and H. Riesenfeldt, *Ber.*, 1927, **60**, [B], 392; A., 369; C. Mannich and O. Walther, *Arch. Pharm.*, 1927, **265**, 1; A., 579; E. Späth and A. Burger, *Ber.*, 1927, **60**, [B], 704; A., 474.

<sup>38</sup> E. Späth and A. Burger, *Monatsh.*, 1926, **47**, 733; A., 1927, 473.

<sup>39</sup> *Ann. Reports*, 1926, **23**, 164.

isomerised to bases of what may be called the protopine type<sup>40</sup> (III), so that each of the three natural alkaloids of the protoberberine type referred to above has its "opposite number" in the protopine series. The first two of these are naturally occurring alkaloids and both have been synthesised by the process just outlined. The third one, cryptopalmatine, has now been synthesised<sup>41</sup> in like manner from palmatine. This process has been carried out successfully also with a number of synthetic protoberberine derivatives and this year it has been tried with protoberberine itself and its 3:11-dimethoxy-derivative, both synthesised for the purpose as described later. With these the process fails because the only anhydro-base produced is of the type B.<sup>42</sup>

The process can also be reversed. As previously reported, there is good ground for regarding corycavine as an alkaloid of the protopine type. The proof of this has been furnished by E. Späth and H. Holter,<sup>43</sup> who have shown that dihydrocorycavine methiodide,  $C_{21}H_{22}O_4NI$ , when heated at  $260^\circ/0.01$  mm. yields two stereoisomeric bases,  $C_{20}H_{19}O_4N$ , m. p.  $140^\circ$  and  $203^\circ$ .<sup>44</sup> Both of these can be completely demethylenated to the corresponding tetrahydric phenolic bases and these on complete methylation furnish *dl*-meso-corydaline and *dl*-corydaline (IV), respectively. Apart from the inherent interest of this transformation, these results confirm the formulæ assigned to corycavine and corycavamine by von Bruchhausen, who represented them as respectively enol- (V) and keto-



(VI) forms of the same substance. The present authors, however, regard corycavine as the keto-form and corycavamine as an

<sup>40</sup> Compare *Ann. Reports*, 1926, **23**, 167, 168.

<sup>41</sup> R. D. Haworth, J. B. Koepfli, and W. H. Perkin, jun., *J.*, 1927, 2261; **A.**, 1096. For a new synthesis of palmatine see *idem, ibid.*, p. 548; **A.**, 472.

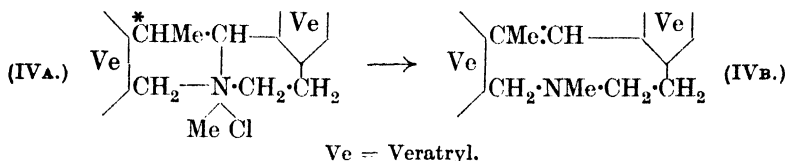
<sup>42</sup> S. N. Chakravarti, R. D. Haworth, and W. H. Perkin, jun., *J.*, 1927, 2265, 2275; **A.**, 1096. See also ref. 51 for similar syntheses, including 2:3-methylenedioxytetrahydropprotoberberine.

<sup>43</sup> *Ber.*, 1927, **60**, [B], 1891; **A.**, 1097.

<sup>44</sup> Compare W. H. Perkin, jun., *J.*, 1918, **113**, 495.

optically active form of corycavine, since it passes into the latter when heated above its melting point.

F. von Bruchhausen and H. Stippler<sup>45</sup> have applied the earlier stages of the same process to producing evidence that the methyl group in corydaline (IV) is in the position shown by the asterisk (IVA) and not substituted for a hydrogen in the methylene group on the left of the nitrogen, as originally suggested by Dobbie and Lauder, a point on which there is now almost general agreement.<sup>46</sup> These authors have converted corydaline through the methochloride (IVA) into the anhydro-base, of which only one form is produced; this they represent by (IVB). This substance on oxidation by permanganate yields 3:4-dimethoxy-2-methylacetophenone, and in addition to this, when the oxidising agent is ozone, 4:5-dimethoxy-2-dimethylaminobenzoic acid, products which lend further support to this location of the methyl group in the parent base.



It will be obvious from the table on p. 168 that if the three natural alkaloids, their tetrahydro-derivatives, and their protopine analogues were completely dealkylated they would yield three tetrahydric phenols, each representative of one of the three series of alkaloids, and that these phenols by suitable re-alkylation could be converted into any one of the three members of the series from which it was derived. This process has already been utilised for such transformations and M. Oberlin<sup>47</sup> has enhanced its possibilities by showing that the dealkylation can be effected by heating the alkaloids with aluminium chloride at temperatures ranging from 140° to 175°, the resulting phenolic bases being recoverable in good yield. In this fashion, papaveraldine has been demethylated to papaveraldoline in the benzylisoquinoline series, berberine has been converted into berberoline, and from the latter palmatine has been produced by methylation, a transformation which had already been effected by other means. E. Späth and E. Mosettig<sup>48</sup> have used this switch-back process this year for the conversion of tetrahydroberberine

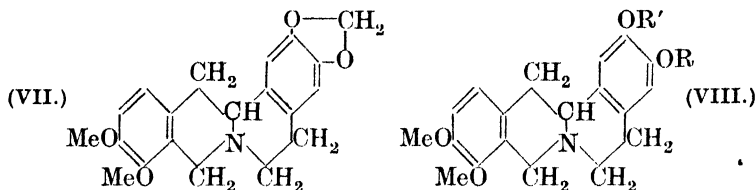
<sup>45</sup> *Arch. Pharm.*, 1927, **265**, 152; **A.**, 683.

<sup>46</sup> Compare, for example, W. Lawson, W. H. Perkin, jun., and R. Robinson, *J.*, 1924, **125**, 631.

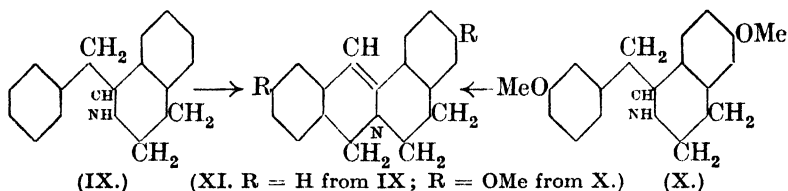
<sup>47</sup> *Arch. Pharm.*, 1927, **265**, 256; **A.**, 681. For other methods, see E. Späth and H. Quietensky, *Ber.*, 1927, **60**, [B], 1882; **A.**, 1066.

<sup>48</sup> *Ber.*, 1927, **60**, [B], 383; **A.**, 368. Compare *Ann. Reports*, 1925, **22**, 151; 1926, **23**, 166.

(VII) into tetrahydropalmatine (VIII;  $R = R' = \text{Me}$ ), tetrahydrocolumbamine (VIII;  $R = \text{Me}, R' = \text{H}$ ) and tetrahydrojatrorrhizine (VIII;  $R = \text{H}, R' = \text{Me}$ ), thus providing further evidence for the formulæ assigned last year to columbamine and jatrorrhizine.<sup>49</sup>



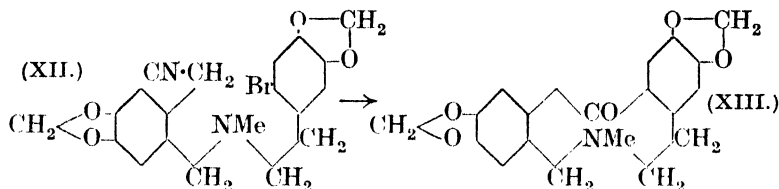
Last year reference was made to work on the synthesis of linear diisoquinoline alkaloids of the paraberine type, which proved much more difficult than that of the "angular" type so far found in nature. S. N. Chakravarti, R. D. Haworth, and W. H. Perkin, jun.,<sup>42</sup> have extended this investigation to the synthesis of dihydroprotoberberine (XI;  $R = \text{H}$ ) and its 3 : 11-dimethoxy-derivative (XI;  $R = \text{MeO}$ ). These were achieved by converting 1-benzyl-1 : 2 : 3 : 4-tetrahydroisoquinoline (IX) and 6-methoxy-1-(3'-methoxybenzyl)-1 : 2 : 3 : 4-tetrahydroisoquinoline (X) into the corresponding formyl derivatives, in which ring closure is effected, presumably in the para-position in the case of the second substance.



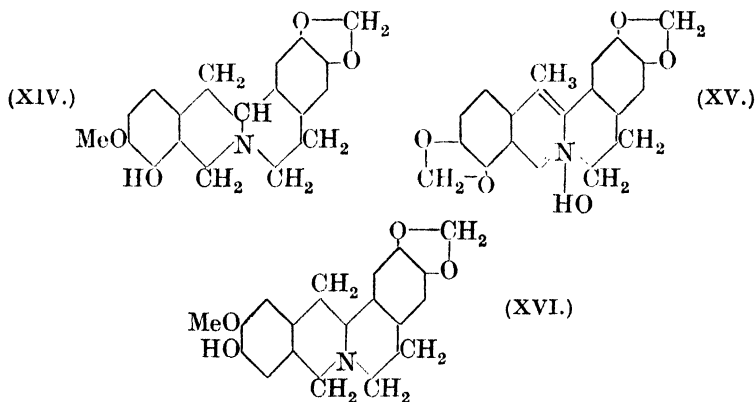
The 3 : 11-dimethoxydihydroprotoberberine was obtained in good yield, but in the synthesis of the dihydroprotoberberine yields were poor and ring closure could only be effected under special conditions. Both substances were reduced to the corresponding tetrahydroprotoberberines and from these by oxidation with iodine the corresponding protoberberinium iodides were obtained and these in turn were decomposed in the normal fashion by potassium hydroxide, giving the corresponding oxyprotoberberines and dihydroprotoberberines (XI), but as already pointed out the conversion into methylanhydro-tetrahydroprotoberberines gave only anhydro-bases of type B (p. 168). The results of this investigation, compared with those of previous work on the synthesis of angular "berberines" containing two alkylated pyrocatechol nuclei, show that the presence of the latter facilitates synthesis, enhances the yellow colour of the

products and raises the melting point, and renders possible the formation of anhydro-bases of type A, containing a ten-membered ring (p. 168).

An interesting attempt<sup>50</sup> has also been made to synthesise the protopine type of alkaloid without passing through the tetrahydroberberine stage, by ring closure of the complex nitrile (XII) to the protopine isomeride (XIII), but neither in this form nor in the corresponding acid (without bromine) could ring closure be effected.



Z. Kitasato<sup>51</sup> has made a number of interesting observations on new alkaloids in this group. The alkaloid nandinine isolated by Eijkmann<sup>52</sup> from *Nandina domestica* is now shown to be *d*-tetrahydroberberrubine (XIV), since it is identical with the dextrorotatory product obtained by the deracemisation of tetrahydroberber-



rubine prepared from berberinium chloride, and since on methylation it furnishes *d*-canadine (tetrahydroberberine).

In addition to berberine and coptisine<sup>53</sup> (p. 168), *Coptis japonica* contains a third alkaloid, worenine; this furnishes a tetrahydro-derivative,  $C_{20}H_{19}O_4N$ , which contains two methylenedioxy-groups and appears from its empirical formula to be a methylcoptisine. The two probable positions for the methyl group are 8 and 13 (I),

<sup>50</sup> T. S. Stevens, *J.*, 1927, 178; *A.*, 265.

<sup>51</sup> *Acta Phytochim.*, 1927, 3, 175; *A.*, 1094.

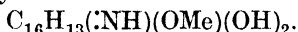
<sup>52</sup> *A.*, 1885, 565.

<sup>53</sup> Compare *Ann. Reports*, 1926, 23, 167.

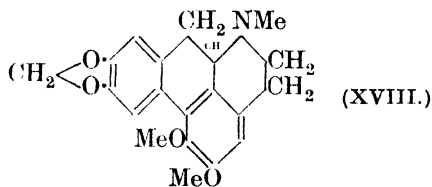
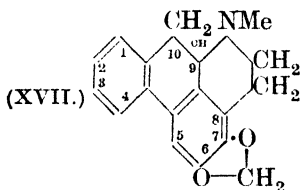
but 8-methylcoptisine prepared by M. Freund's method <sup>54</sup> is different from tetrahydroworenine, which leaves the 13-position as probable (XV). Tetrahydroworenine ought therefore on demethylenation and methylation (p. 170) to yield corydaline (IV).

Arising out of the work on nandine, the synthesis has been effected by the same author of tetrahydro*pseudoberberine*, which on methylation gives tetrahydro*pseudoberberine*.<sup>55</sup>

Mention may also be made of preliminary work on two other alkaloids which from their botanical relationships may belong to this group, *viz.*, oxyacanthine<sup>56</sup> and coclaurine,<sup>57</sup>



*Phenanthrenoisoquinolines*.—Z. Kitasato has obtained from *Nandina domestica* two other alkaloids which belong to this group, *viz.*, domesticine and isodomesticine, and are probably respectively the 2-hydroxy-3-methoxy- and the 3-hydroxy-2-methoxy-derivatives of the substance represented by formula (XVII). On methylation,



both furnish the same methyl ether, named domesticine (XVII with MeO in 2 and 3). Oxidation of domesticine yields 4 : 5-methylene-dioxybenzene-1 : 2 : 3-tricarboxylic acid. *epi*Dicentrine (XVIII) has been synthesised by the same author by R. Pschorr's <sup>58</sup> method from homopiperonylhomoveratrylamine and deracemised through the *d*-tartrate.

*Morphine Sub-group*.—It was mentioned last year that the two points on which attention is mainly concentrated in discussions on the formulæ of morphine, codeine and thebaine are the position of the ethylenic linking in codeine and the point of attachment of the carbon end of the ethanamine chain. Two further papers published since then <sup>59</sup> favour the 7 : 8 position for the ethylenic linking, so that agreement on this point is becoming general. The second

<sup>54</sup> *Ber.*, 1904, **37**, 4673; *A.*, 1905, i, 151.

<sup>55</sup> *Ann. Reports*, 1924, **21**, 134.

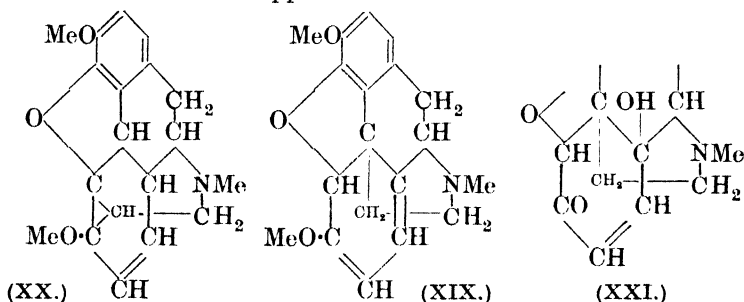
<sup>56</sup> E. Späth and A. Kolbe, *Ber.*, 1925, **58**, [B], 2280; *A.*, 1926, 821; J. Gadamer and W. von Bruchhausen, *Arch. Pharm.*, 1926, **264**, 193; *A.*, 1926, 627.

<sup>57</sup> H. and T. Kondo, *J. Pharm. Soc. Japan*, 1925, No. 524, 876; *A.*, 1926, 82.

<sup>58</sup> *Ber.*, 1904, **37**, 1926; *A.*, 1904, i, 611.

<sup>59</sup> J. von Braun and R. S. Cahn, *Annalen*, 1926, **451**, 55; *A.*, 1927, 266; C. Schöpf and collaborators, *ibid.*, 1927, **452**, 211; *A.*, 472.

paper produces much new evidence supporting Robinson and Gulland's formulæ for codeine and thebaine, in preference to those put forward by Wieland and Kotake. Thus a well-crystallised tetrahydrothebaine has been obtained by reduction of thebaine under conditions which imply the presence of two ethylenic linkings as in Robinson and Gulland's formula (XIX), but in which a bridge, as suggested by Wieland and Kotake (XX), would probably remain unaffected.<sup>60</sup> Similar support is afforded to Robinson and Gulland's



representation of hydroxycodone (XXI), produced by the action of hydrogen peroxide on thebaine. The little-known alkaloid porphyroxine, obtained from Indian opium, has been assigned to this sub-group by a curious formulation suggested by J. N. Rakshit.<sup>61</sup>

*Ipecacuanha Alkaloids.*—It has been known since 1914 that emetine and the subsidiary alkaloids associated with it are *isoquinoline* derivatives, because emetine on oxidation furnishes 6 : 7-dimethoxy*isoquinoline*-1-carboxylic acid and the close relationship of the subsidiary alkaloids to emetine has been clearly established.<sup>62</sup> E. Späth and W. Leithe<sup>63</sup> found that oxidation of emetine in faintly alkaline solution gave 1-keto-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydro*isoquinoline*, so that unless unusual dehydrogenation occurs in this operation the latter must come from a second *isoquinoline* nucleus, and support for this view was found in the fact that under suitable conditions of oxidation much more *m*-hemipinic acid is formed than is normally produced by oxidation of such bases as palmatine and papaverine containing only one *isoquinoline* nucleus. These authors therefore put forward the skeleton formula (XXII) for emetine with the suggestion that the tertiary nitrogen atom forms part of a piperidine ring. Proceeding on the lines of his suggested mechanism for the formation of alkaloids in plants,<sup>64</sup> Robinson suggested in 1925 formula (XXIII),

<sup>60</sup> For references and numbering of rings, see *Ann. Reports*, 1926, **23**, 173.

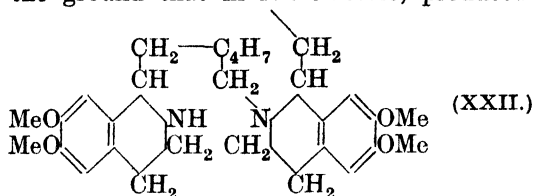
<sup>61</sup> *J.*, 1919, **115**, 456; *Ber.*, 1926, **59**, [B], 2473; *A.*, 1927, 64.

<sup>62</sup> F. H. Carr and F. L. Pyman, *J.*, 1914, **105**, 1591; F. L. Pyman, *J.*, 1917, **111**, 419; 1918, **113**, 222.

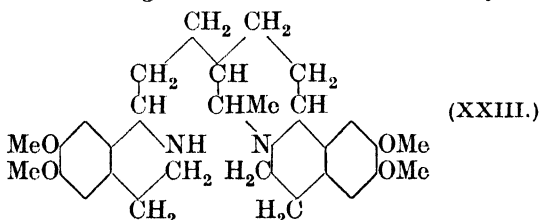
<sup>63</sup> *Ber.*, 1927, **60**, [B], 688; *A.*, 471.

<sup>64</sup> *J.*, 1917, **111**, 888.

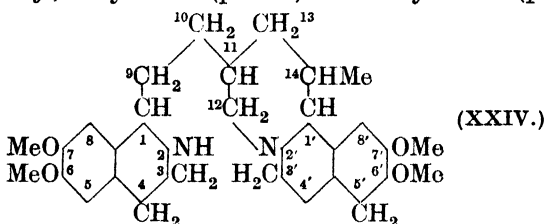
which W. H. Brindley and F. L. Pyman<sup>65</sup> have modified to (XXIV), chiefly on the ground that in rubremetine, produced by gentle



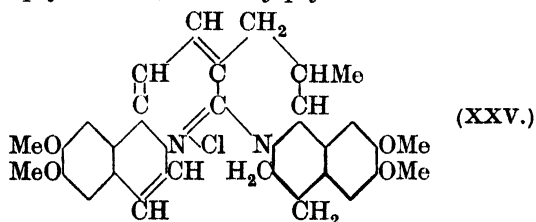
oxidation of emetine in the course of which 8 atoms of hydrogen are lost, one nitrogen becomes quadrivalent and the other loses its basicity. These changes are better accounted for by the berberine-



like formula (XXV) for rubremetinium chloride, which is more easily derivable from (XXIV), loss of basicity being accounted for by amidine formation, an ethylenic linking connecting N (2) to C (12). This position for the methyl group also has the advantage of conforming with the location of such groups in other *isoquinoline* alkaloids, *e.g.*, corydaline (p. 170) and corycavine (p. 169).



Cephæline, of which emetine is a monomethyl ether, probably has a phenolic hydroxyl at 6, and partly on the results of new experimental work, closely related formulæ are put forward by the same authors for psychotrine, *O*-methylpsychotrine and emetamine.



<sup>65</sup> *J.*, 1927, 1067; *A.*, 682. Robinson's formula is published in this paper.



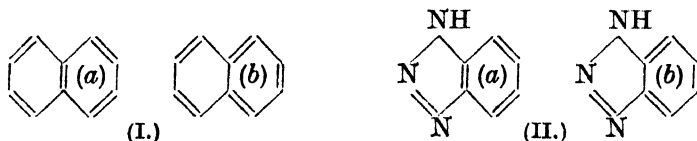
*Azoles.*

Much important work has been published on these products, but for the most part it follows the lines referred to in other recent reports of this series under the headings of diazoles, oxazoles, pyrazoles, and indazoles.

In the course of an elaborate investigation of the "benzoid" or "naphthoid" character of dicyclic systems (one ring homo- and the second hetero-cyclic), K. Fries with a number of collaborators<sup>66</sup> has subjected benzotriazoles, benziminazoles, benzthiazoles, benzisothiazoles, benzthiodiazoles, and indazoles to a series of simple critical reactions and examined the products. Those compounds are regarded as naphthoid in which there is evidence of two types of ortho-positions corresponding to the  $\alpha$ - and  $\beta$ -positions in the naphthalene series.

The results show that only the benzotriazoles regularly exhibit naphthoid behaviour, although the benzthiodiazoles and the indazoles also have a well-marked tendency in the same direction. The other systems are definitely benzoid.

In seeking an explanation of these results, the author points out that of the two pairs of formulæ (Ia, b) and (IIa, b) the *b* type can be regarded as possessing a potential dihydride structure, homo-cyclic in (Ib) and heterocyclic in (IIb). Dihydrobenzenes are unstable and consequently naphthalene probably always exists in the *a* form. On the other hand, the dihydro-derivatives of iminazoles and thiazoles are stable and easily formed, and those of the triazoles are unknown. In general, if the dicyclic systems studied be supposed to exist as equilibrium mixtures of types (*a*) and (*b*), naphthoid behaviour, as defined above, will be predominant when the equilibrium amount of (*b*) is very small, and this will generally be the case when the dihydro-derivative of the simple parent heterocyclic ring is readily dehydrogenated.



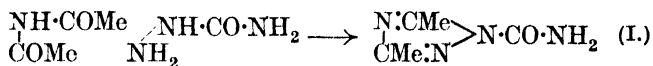
*Triazoles.*—This group of heterocyclic compounds has received a great deal of attention during the last four years, particularly as regards methods of formation, preparation of derivatives such as the triazolealdehydes,<sup>67</sup> and demonstration of the surprising stability of the ring system, and the influence upon this of various substituents.

<sup>66</sup> *Annalen*, 1912, **389**, 305; 1914, **404**, 50; 1927, **454**, 121; *A.*, 1912, **i**, 556; 1914, **i**, 569; *A.*, 1927, 778.

<sup>67</sup> C. A. Rojahn and H. Triefoff, *Annalen*, 1925, **445**, 296; *A.*, 1926, 78.

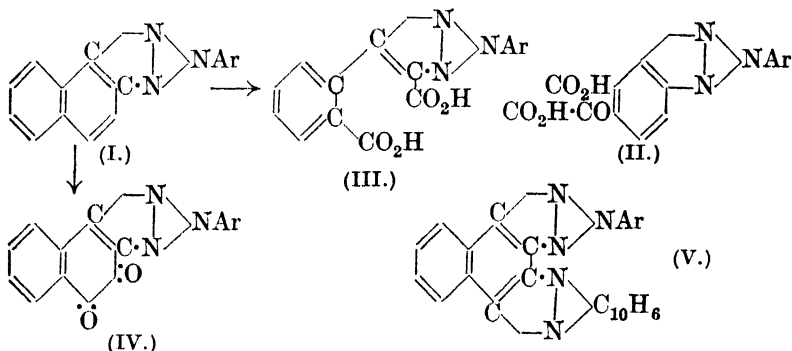
These points can be illustrated by many of the papers published during the period, but only a selection can be referred to.

K. Brunner and J. Medweth<sup>68</sup> have produced confirmatory evidence for the view that the synthesis of dimethyltriazole from diacetamide and semicarbazide takes place through 3 : 5-dimethyl-1 : 2 : 4-triazole-1-carboxylamide (I), which then reacts with a second



molecule of semicarbazide to form dimethyltriazole and hydrazoformamide. In like manner, diacetamide and phenylhydrazine produce 1-phenyl-3 : 5-dimethyl-1 : 2 : 4-triazole. The intermediate product (I) has been synthesised by the action of potassium cyanate on a solution of 3 : 5-dimethyl-1 : 2 : 4-triazole at  $-5^\circ$ ; it regenerates the simple dialkyltriazole in presence of warm alcohol, water, or aniline with the expected specific by-products in each case.

The stability of the triazole ring is clearly demonstrated by the work of G. Charrier and his colleagues on the oxidation of the 2-aryl- $\alpha\beta$ -naphthatriazoles (I). These substances are converted by alkaline permanganate<sup>69</sup> into dibasic acids, which were at first regarded as 2-aryltriazolephthalonic acids (II), but were subsequently shown to have the structure represented by type formula (III). Triazoles of



the same group are oxidised by potassium dichromate and sulphuric acid<sup>70</sup> to *o*-quinones (IV), which closely resemble phenanthraquin-

<sup>68</sup> *Monatsh.*, 1926, **47**, 741; *A.*, 1927, 468. For applications of the general method, see *ibid.*, 1926, **47**, 747, 791; 1927, **48**, 37, 391; *A.*, 1927, 468, 777, 1090.

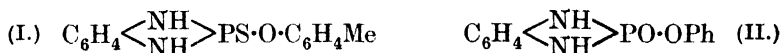
<sup>69</sup> *Gazzetta*, 1923, **53**, 829, 862; 1924, **54**, 647; 1925, **55**, 7, 745; *A.*, 1924, i, 329, 334; 1925, i, 76, 589; *A.*, 1926, 307. Compare A. Beretta, *ibid.*, 1925, **55**, 788; *A.*, 1926, 182.

<sup>70</sup> *Gazzetta*, 1924, **54**, 610; 1926, **56**, 191, 196; *A.*, 1924, i, 1351; *A.*, 1926, 848; *Atti R. Accad. Lincei*, 1926, [vi], **4**, 312; *A.*, 1927, 63.

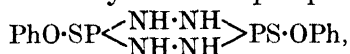
ones in physical properties and in reactions, producing, for example, azines (V) by condensation with *o*-diamines.

Hydrogen peroxide converts the triazoles into amine oxides, but it is not yet certain to which of the three nitrogens the oxygen atom becomes attached.<sup>71</sup>

"*Diazphospholes*."—W. Autenrieth and collaborators<sup>72</sup> have prepared a series of substances for which they have coined this name. They are produced by the action of thiophosphoryl dichlorides on diamines, thus:—*p*-tolylloxythiophosphoryl dichloride and *o*-phenylenediamine yield *p*-tolylloxy-*P*-thiodihydrobenzodiazphospholium (I). When oxyphosphoryl dichlorides are used, as, for example,



phenoxyphosphoryl dichloride, on *o*-phenylenediamine, analogous compounds containing oxygen in place of sulphur are produced, in this instance phenoxy-*P*-oxodihydrobenzodiazphospholium (II), which is stable to water and acids but is hydrolysed by alkalis. When diamines are replaced by hydrazine, the rings formed contain nitrogen and phosphorus only; thus phenoxythiophosphoryl dichloride (1 mol.) with hydrazine hydrate (2 mols.) produces *PP'*-diphenoxy-*PP'*-dithiotetrahydrotetraazidiphosphonium,



the oxygen analogue of which is obtainable by the use of phenoxyphosphoryl dichloride in like manner.

#### *Diazines.*

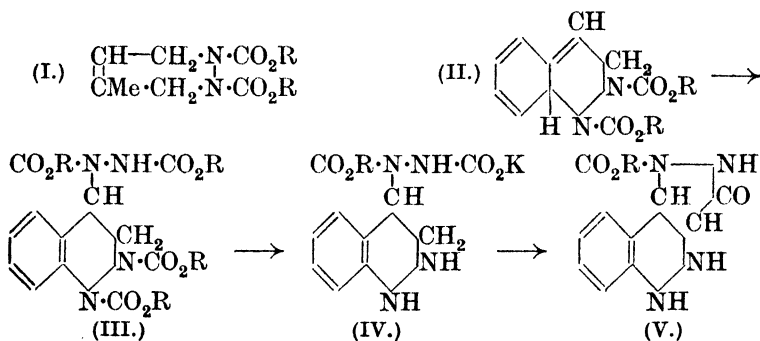
Much of the work in this section relates as usual to the formation and transformation of diketopiperazines in connexion with the degradation of proteins. P. Pfeiffer, O. Angern, and L. Wang,<sup>73</sup> dealing with "molecular compounds" formed by these substances with amino-acids, point out that as such compounds are formed only with secondary or primary amines, whether carboxylated or not, and never with tertiary amines, the imino- or amino-group must provide the residual affinity for engagement with one of the keto-groups of the diketopiperazine, and formulæ based on this assumption are suggested.

<sup>71</sup> *Gazzetta*, 1923, **53**, 462; 1925, **55**, 11; 1926, **56**, 207; *A.*, 1923, i, 1140; 1925, i, 589; *A.*, 1926, 848. Compare M. and M. Giua, *ibid.*, 1923, **53**, 165; *A.*, 1923, i, 672; A. Angeletti, *ibid.*, 1923, **53**, 672; *A.*, 1924, i, 93.

<sup>72</sup> [With O. Hildebrand] *Ber.*, 1898, **31**, 1094; *A.*, 1898, i, 419; [with W. Meyer] *Ber.*, 1925, **58**, [B], 848; *A.*, 1925, i, 989; [with E. Bölli] *ibid.*, p. 2144; *A.*, 1925, i, 1468. Compare W. Strecker and H. Heuser, *Ber.*, 1924, **57**, [B], 1364; *A.*, 1924, i, 1159.

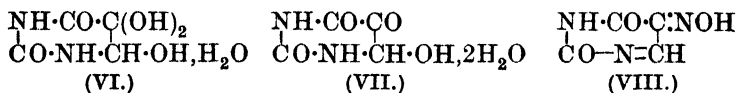
<sup>73</sup> *Z. physiol. Chem.*, 1927, **164**, 182; *A.*, 676.

Although the work of O. Diels and K. Alder <sup>74</sup> on the addition of ethyl azodicarboxylate to unsaturated hydrocarbons containing conjugated linkings is not primarily concerned with the chemistry of heterocyclic substances, interesting substituted pyridazines result in some instances from these reactions and justify allusion to it here. Thus isoprene gives rise to ethyl 5-methyl-1:2:3:6-tetrahydro-1:2-pyridazine-1:2-dicarboxylate (I) and myrcene forms a strictly analogous product. Styrene, on the contrary, in which the conjugated linkings are partly cyclic and partly extra-cyclic, probably combines first with one molecule of the methyl ester to form a reduced benzopyridazine (II), which at once regains benzenoid character by reducing and combining with a second molecule of the ester to form methyl 4-hydrazino-1:2:3:4-tetrahydrocinnoline-*NN'**N''N'''*-tetracarboxylate (III), which behaves as a saturated substance and on hydrolysis by potassium hydroxide gives potassium 4-carbomethoxyhydrazinotetrahydrocinnoline-*ω*-carboxylate (IV) and this with acetic acid is converted into methyl *ar*-hexahydrocinnolino-1:2-pyrazol-3-one-1-carboxylate (V).



Among heterocyclic substances, pyrrole reacts violently with ethyl azodicarboxylate, forming an ill-defined product, thiophen is inert, and furan reacts readily.

H. Biltz and his collaborators, <sup>75</sup> continuing their work on pyrimidine compounds, have produced a considerable body of evidence for the view that isodialuric acid is a 5:5:6-trihydroxy-5:6-dihydrouracil (VI), and not a simple isomeride (VII) of dialuric acid



containing two molecules of water of crystallisation. For example, it forms dialkyl ethers in which one of the alkyl groups must be in

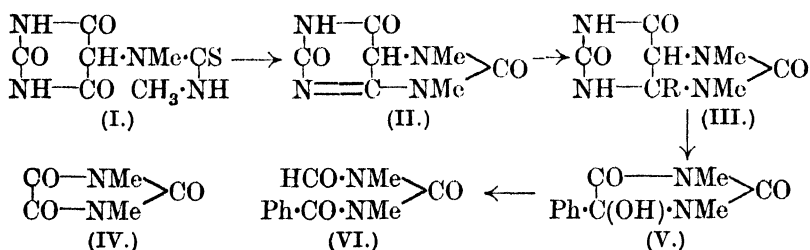
<sup>74</sup> *Annalen*, 1926, **450**, 237; *A.*, 1927, 159.

<sup>75</sup> [With H. Paetzold and P. Nachtwey] *Annalen*, 1927, **452**, 67; *A.*, 259.

position 5 and the other in 5 or 6. These ethers can be methylated by diazomethane on both nitrogens and with carbamide they furnish 1 : 3-dimethyluric acids. Further, the acid yields with excess of hydroxylamine an oxime anhydride (VIII).

### Purines.

The same group of workers have investigated the formation and degradation of 7 : 9-dimethyl- $\Delta^{3:4}$ - and 3 : 9-dimethyl- $\Delta^{5:7}$ -isouric acids. The former (II) results from the oxidation of 7 : 9-dimethyl-8-thiopseudouric acid (I) with iodine in presence of sodium hydrogen carbonate. It forms salts with acids, probably through the tertiary nitrogen atom, and with alkalis by replacement of the hydrogen atom of the imino-group, for which, however, alkyl groups, presented in the form of the usual reagents, cannot be substituted. Perhaps the most interesting of its many reactions is that with organic acids: the acid is broken up, carbon dioxide is liberated, the hydrogen atom of the carboxyl group attaches itself to the nitrogen atom at position 3, and the residual radical ( $R = H$  from formic acid,  $Me$  from acetic acid,  $Ph$  from benzoic acid) is bestowed on carbon atom 4, giving rise to a 7 : 9-dimethyl-3 : 4-dihydrouric acid (III). These products, like the original substance, are oxidised to dimethylparabanic acid (IV) except in the case where the phenyl group enters at position 4, rendering the product stable to nitric acid, although it can be oxidised by chromic acid to 5-hydroxy-5-phenyl-1 : 3-dimethylhydantoin (V), the ring of which opens in contact with nitric acid, producing *N*-formyl-*N'*-benzoyldimethyl-carbamide <sup>76</sup> (VI).

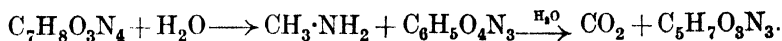


The isomeric substance, 3 : 9-dimethyl- $\Delta^{5:7}$ -isouric acid (VII), was obtained in the course of work arising out of the chlorination of 3 : 9-dimethyluric acid.<sup>77</sup> Degradation of some of the resulting products or the direct action of chlorine on 3 : 9-dimethyl- $\Delta^{5:7}$ -isouric acid suspended in water gives rise to 5-hydroxy-1-carbamyl-3-methylhydantoin (VIII), about the constitution of which there

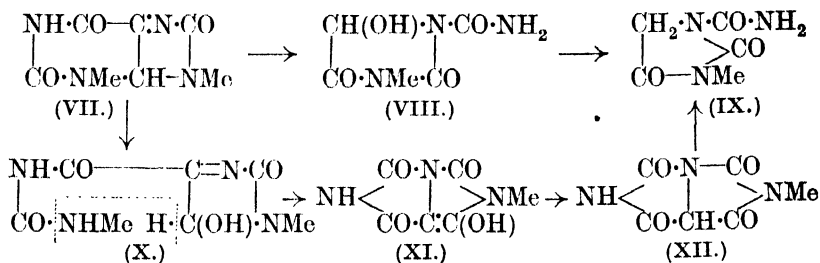
<sup>76</sup> H. Biltz and H. Bülow, *Annalen*, 1927, **457**, 103; **A.**, 1090.

<sup>77</sup> H. Biltz, H. Krzikalla, and, in part, K. Slotte, *ibid.*, p. 131; **A.**, 1091.

can be little doubt, since it is oxidised by chromic acid to methylparabanic acid (IV, with one Me group) and is reduced by hydriodic acid to 3-methylhydantoin and its 1-carbamyl derivative (IX), which has since then been synthesised from 3-methylhydantoin by the action of carbamyl chloride under special conditions.<sup>78</sup> Hydrolysis of the product by acids gives rise to reactions which may be represented as follows :



The terminal substance,  $\text{C}_5\text{H}_7\text{O}_3\text{N}_3$ , is again 1-carbamyl-3-methylhydantoin (IX) and its formation is believed to take place as shown by formulæ (X), (XI), and (XII), rupture occurring between positions



3 and 4 to give (X), which then loses methylamine, forming (XI), which is then rearranged to 2-methylhydantoinohydantoin (XII),  $\text{C}_6\text{H}_5\text{O}_4\text{N}_3$ , and this is eventually hydrolysed to 1-carbamyl-3-methylhydantoin (IX). Reference may also be made to two syntheses of 8-methyl-7-ethylxanthine starting from glyoxaline derivatives.<sup>79</sup>

### Organo-metallic Compounds.

Since 1921, when substances of this type last received extended notice in this Report, there has been remarkable activity in this field of work, mainly from three points of view, the preparation of therapeutic substances,<sup>80</sup> the study of colloids, and the demonstration of the asymmetrical arrangement of radicals attached to arsenic or other metallic atoms.<sup>81</sup> In all these directions progress

<sup>78</sup> H. Biltz and Fraulein D. Heidrich, *Annalen*, 1927, **457**, 190; *A.*, 1093.

<sup>79</sup> F. M. Diaz de Plaza, *Anal. Fis. Quím.*, 1926, **24**, 731; F. Montequi, *ibid.*, 1927, **25**, 182; *A.*, 469, 979.

<sup>80</sup> See, for example, H. King and collaborators, *J.*, 1924, **125**, 2595; 1925, **127**, 2632, 2701; 1926, 817, 1355; 1927, 1049; *A.*, 1925, i, 319; *A.*, 1926, 186, 187, 746, 851; 1927, 684; *J. Pharm. Exp. Ther.*, 1926, **28**, 341; *A.*, 1926, 1173; G. Giemsa and C. Tropp, *Ber.*, 1926, **59**, [B], 1776; *A.*, 1926, 1162; E. Fourneau and colleagues, *Bull. Soc. chim.*, 1927, [iv], **41**, 499; *A.*, 580.

<sup>81</sup> J. A. Aeschlimann, *J.*, 1925, **127**, 811; *A.*, 1925, i, 706; W. H. Mills and R. Raper, *ibid.*, p. 2479; *A.*, 1926, 186.

has been made, but in comparatively few cases are the results of such a character as to come strictly within the scope of this Report.

The arsenic acid residue has been attached to a great variety of cyclic structures, including phenylglyoxaline,<sup>82</sup> phenylbenzthiazole,<sup>83</sup> benzoxazolone,<sup>84</sup> 9-methylcarbazole,<sup>85</sup> quinoline,<sup>86</sup> and certain of the cinchona alkaloids,<sup>87</sup> but only in a few instances has this or an allied residue been attached to a carbon atom in a heterocyclic ring, for example, in thiophen,<sup>88</sup> pyridine<sup>89</sup> or pyrrole.<sup>90</sup> In most of these cases the arsenical residue has been inserted by well-known methods such as treatment with arsenic acid, oxidation of chloroarsines, or by the Bart reaction applied to appropriate diazotised amines, and in a few instances the heterocyclic structure has been built upon a preformed homocyclic arsenic acid, for example, in the production of a series of quinoxaline-6-arsinic<sup>91</sup> acids, the formation of *pp'*-di-4-carboxy-2-quinolylarsenobenzene,<sup>92</sup> and in a protected process for the conversion of 4:4'-diamino-3:3'-dihydroxyarsenobenzene into benzoxazolone derivatives by the action of carbonyl chloride.<sup>84</sup>

Considerable progress has also been made in the study of arsenical analogues of heterocyclic nitrogen compounds. Thus J. A. Aeschlimann, N. D. Lees, N. P. McClelland, and G. N. Nicklin<sup>93</sup> have shown that diphenylarsinic acid on treatment with warm sulphuric acid undergoes ring closure to *oo'*-diphenyllylenearsinic acid (I), which on reduction by sulphur dioxide in presence of hydrochloric acid yields *oo'*-diphenyllylenechloroarsine, and this through the

<sup>82</sup> I. E. Balaban and H. King, *J.*, 1925, **127**, 2701; *A.*, 1926, 187; I. E. Balaban, *J.*, 1926, 569; *A.*, 1926, 623; compare *Ann. Reports*, 1926, **23**, 175; see also *Brit. Pat.* 256,243; *B.*, 1927, 670.

<sup>83</sup> M. T. Bogert and H. B. Corbitt, *Proc. Nat. Acad. Sci.*, 1925, **11**, 768; *A.*, 1926, 187.

<sup>84</sup> *Brit. Pat.* 214,628, 239,951, 257,361, 261,133; *B.*, 1925, 149; *A.*, 1925, i. 1470; *B.*, 1926, 932; 1927, 125; E. Fourneau and J. and (Mme.) J. Tréfouel, *Bull. Soc. chim.*, 1927, [iv], **41**, 448; *A.*, 555.

<sup>85</sup> H. Burton and C. S. Gibson, *J.*, 1927, 2387; *A.*, 1098.

<sup>86</sup> A. Binz and C. R  th, *Annalen*, 1927, **453**, 238; *A.*, 580.

<sup>87</sup> F. X. Erben with N. Schniderschitsch and others, *Ber.*, 1925, **58**, [B], 693, 2854; *A.*, 1925, i, 707; *A.*, 1926, 188.

<sup>88</sup> C. Finzi, *Gazzetta*, 1925, **55**, 824; *A.*, 1926, 186.

<sup>89</sup> A. Binz and C. R  th, *Annalen*, 1927, **455**, 127; *A.*, 1927, 890; compare *Brit. Pat.* 250,287, 250,577, 263,142; *B.*, 1926, 512; 1927, 670, 734.

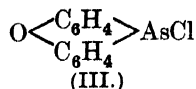
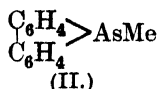
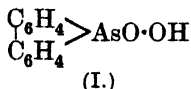
<sup>90</sup> H. Fischer and R. M  ller, *Z. physiol. Chem.*, 1925, **148**, 155; *A.*, 1926, 75.

<sup>91</sup> W. L. Lewis and others, *J. Amer. Chem. Soc.*, 1924, **46**, 2058; 1926, **48**, 949; *A.*, 1924, i, 1245; *A.*, 1926, 628.

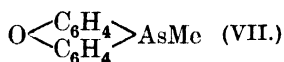
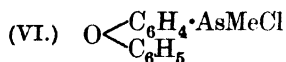
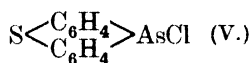
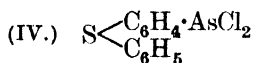
<sup>92</sup> R. Adams and collaborators, *ibid.*, 1925, **47**, 826, 3058; *A.*, 1925, i, 706; *A.*, 1926, 187.

<sup>93</sup> *J.*, 1925, **127**, 66; *A.*, 1925, i, 319; compare H. Gottlieb-Billroth, *J. Amer. Chem. Soc.*, 1927, **49**, 482; *A.*, 368.

corresponding iodoarsine can be converted into *oo'*-diphenylene-methylarsine (II) by the action of magnesium methyl iodide.



The constitution of 10-chlorophenoxarsine (III), first prepared in 1918, has been established by its synthesis from *o*-phenoxyphenyldichloroarsine, hydrogen chloride being eliminated when this substance is distilled at 10 mm. or heated at 200° in a current of carbon dioxide.<sup>94</sup> This process proceeds so smoothly that it has been applied to the investigation of ring closure in the *o*-, *m*-, and *p*-chloro-derivatives of *o*-phenoxyphenyldichloroarsine. The results show that the chief factor influencing ring closure in these cases is steric hindrance, modified by polar effects due to the oxygen and the substituent chlorine atom,<sup>95</sup> and the same influences are believed to determine whether sulphonation, ring closure, or both, occur in the action of warm sulphuric acid on *o*-phenoxyphenylarsinic acid and its chloro-compounds. When oxygen is replaced by sulphur, as in *o*-phenylthiolphenyldichloroarsine (IV), ring closure takes place only to the extent of 20% (as against 60% in the case of *o*-phenoxyphenyldichloroarsine) with the formation of 10-chlorophentharsine (V) and with *o*-phenoxyphenylmethylchloroarsine (VI) only 10% of the possible loss of hydrogen chloride, with some methyl chloride, occurs and the expected 10-methylphenoxarsine (VII) could not be detected in the reaction products.



The latter was, however, made by treating 10-chlorophenoxarsine (III) with magnesium methyl iodide<sup>96</sup> by what was claimed to be an improved method of general applicability, though this has not been confirmed by another worker for the preparation of 10-ethyl- and 10-phenyl-phenoxarsines.<sup>97</sup>

Phenarsazine, a war product with a brief but tangled history,<sup>98</sup> and its derivatives have been the subject of a number of papers

<sup>94</sup> E. E. Turner and A. B. Sheppard, *J.*, 1925, **127**, 544; *A.*, 1925, **i**, 705. For system of numbering oxarsine and thioarsine rings, see *A.*, 1926, 852.

<sup>95</sup> E. Roberts and E. E. Turner, *ibid.*, p. 2004; *A.*, 1925, **i**, 1339.

<sup>96</sup> *Idem*, *ibid.*, 1926, 1207; *A.*, 1926, 852. Compare ref. 1, p. 185.

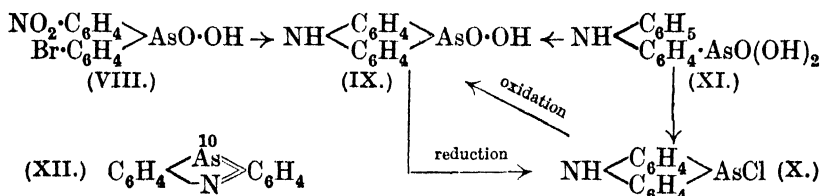
<sup>97</sup> J. A. Aeschlimann, *ibid.*, 1927, 413; *A.*, 368.

<sup>98</sup> H. Burton and C. S. Gibson, *J.*, 1924, **125**, 2275; 1926, 450; *A.*, 1925, **i**, 84; *A.*, 1926, 418.



by C. S. Gibson and his colleagues, which have improved technique and added considerably to our knowledge of these substances. "Phenarsazine chloride" is shown to have the constitution assigned to it by H. Wieland and W. Rheinheimer<sup>99</sup> by a synthesis starting from 2-bromo-2'-nitrodiphenylarsinic acid (VIII) produced by coupling *o*-bromophenylarsenious oxide with diazotised *o*-nitroaniline. This product is reduced to the corresponding amino-compound, which may then be subjected to ring closure by heating it in solution in amyl alcohol with potassium carbonate and a little copper powder; the phenarsazinic acid (IX) thus formed may be reduced with sulphur dioxide in presence of hydrochloric acid and a little iodine to the desired substance (X), now renamed 10-chloro-5:10-dihydrophenarsazine, which clearly defines its relation to phenarsazine<sup>98</sup> (XII).

Ring closure has also been effected at the nitrogen atom of the heterocyclic ring by condensing either *o*-bromophenylarsinic acid with aniline or *o*-aminophenylarsinic acid with bromobenzene; diphenylamine-*o*-arsinic acid (XI) then results in 50 and 5% yields, respectively. This undergoes ring closure to phenarsazinic acid (IX) hydrochloride when boiled with concentrated hydrochloric acid and to 10-chloro-5:10-dihydrophenarsazine ("phenarsazine chloride") (X) when reduced with sulphur dioxide in presence of hydrochloric acid and iodine. Further, the change (X) to (IX) can be effected by oxidation and reversed by the special sulphur dioxide reduction (see above).

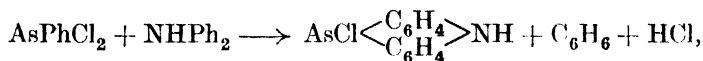


The second mode of ring closure, that is, at the nitrogen atom, has been investigated, first as to the relative advantage, for preparation of the initial substituted diphenylaminearsinic acid, of the insertion of the bromine atom (and therefore inversely of the amino-group) in the phenylarsinic acid or in the hydrocarbon ring, and, secondly, as to the limiting conditions for simple ring closure. The decision as to which of the two reagents to be condensed is to have the bromine atom depends upon the reactivity of the latter in the two possible bromine compounds. All the substituted diphenylaminearsinic acids so far examined condense satisfactorily except *N*-methyldiphenylamine-*o*-arsinic acid, which furnishes

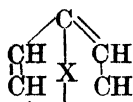
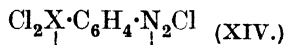
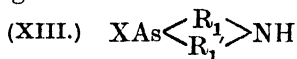
<sup>99</sup> *Annalen*, 1921, 423, 1; *A.*, 1921, i, 371.

10-chloro-5-10-dihydrophenarsazine (X) in small quantity instead of the expected 5-methyl derivative, probably because in this case ring closure is largely inhibited by steric hindrance and such small amount of condensation product as may be formed loses methyl chloride.<sup>1</sup>

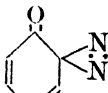
The reaction by which 10-chloro-5:10-dihydrophenarsazine is most easily produced, namely, heating together arsenious chloride and diphenylamine, alone or in presence of a solvent, also takes place with homologues of diphenylamine and certain of their derivatives and it has been sought to extend it to dichloroarsines  $R \cdot AsCl_2$  in the hope of obtaining substances of type (XIII,  $X =$  univalent hydrocarbon radical), but it was found that, when diphenylamine was treated with phenyldichloroarsine, the reaction proceeded in accordance with the equation



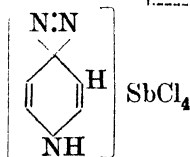
quantitative yields of 10-chloro-5:10-dihydrophenarsazine being obtained, and under suitable conditions the elimination of benzene could be demonstrated. The reaction proceeds in the same sense with homologues of diphenylamine.<sup>2</sup> In view of these results, it seemed unlikely that the condensation of  $\beta$ -chlorovinyl dichloroarsine with diphenylamine could lead, as stated by W. L. Lewis and H. W. Stigler,<sup>3</sup> to the formation of chlorovinylphenarsazines, and repetition of the work shows that in these cases also the reaction proceeds in the sense of the foregoing equation, vinyl chloride being evolved.



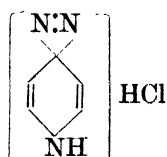
(XV.)



(XVI.)



(XVII.)



(XVIII.)

A number of interesting arsenical, antimonial and bismuth derivatives of diazonium compounds have been described, the constitution of which is still under discussion. H. Schmidt and F. Hoffmann<sup>4</sup> have described diazotised aminophenylarsine dichlorides and aminophenylstibine dichlorides to which they attribute

<sup>1</sup> C. S. Gibson and J. D. A. Johnson, *J.*, 1927, 2499; *A.*, 1210. Compare refs. 95 and 96.

<sup>2</sup> H. Burton and C. S. Gibson, *J.*, 1926, 464, 2241; *A.*, 1926, 419, 1162.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1925, 47, 2546; *A.*, 1925, i, 1470.

<sup>4</sup> *Ber.*, 1926, 59, [B], 555, 560; *A.*, 1926, 533.

formula (XIV;  $X = \text{As}$  or  $\text{Sb}$ ). The former, on treatment with a suspension of sodium hydrogen carbonate in water, is converted into *p*-phenylenearsinic acid (XV;  $X = \text{AsO}\cdot\text{OH}$ ), which on reduction with sulphur dioxide in presence of iodine yields *p*-phenylenechloroarsine (XV;  $X = \text{AsCl}$ ).

3-Amino-4-hydroxyphenylarsinic acid, when similarly treated, furnishes a substance,  $\text{C}_6\text{H}_4\text{ON}_2\text{Cl}_3\text{As}$ , which readily loses hydrogen chloride and is converted into the quinonediazide (XVI).

Crystalline compounds of antimony trichloride with diazonium salts containing groups of basic character have been described by W. H. Gray.<sup>5</sup> Owing to their sparing solubility and the still smaller solubility of the basic antimony chloride formed by the action of water upon them, they provide a means of isolating the corresponding diazonium salts in cases where the latter are both very soluble and readily hydrolysed, for example, *p*-acetamidobenzenediazonium chloride. The hydrolytic product of the latter is shown to be the hydrochloride of the hypothetical *p*-diazoimino-benzene (XVIII), which was isolated through its sparingly soluble antimony trichloride compound (XVII) in the same way. This is the parent substance of the acyl-*p*-diazoimides, which have been extensively studied by G. T. Morgan and his collaborators.

One of the principal incentives to the preparation of organo-metallic compounds for the last twenty years, especially in relation to arsenic and antimony and to a much less extent bismuth, has been the fact that variation in the nature of the organic component, in which the metallic residue is inserted, usually led to variation in pharmacological action. Evidence is now steadily accumulating that the complex compounds which these metals form with the polyhydroxycarboxylic acids also afford a possibility of variation and already a considerable amount of work has been devoted to the preparation of such substances and to suggestions regarding their constitution,<sup>6</sup> but most of these views are as yet too speculative for useful comment.

*Mercury and Gold Compounds.*—The prevalent impression that the benzene ring always mercurates in *o*-, *p*-positions no matter what substituent may be present has been corrected by a number of workers. O. Dimroth<sup>7</sup> has shown that in the mercuration of

<sup>5</sup> J., 1926, 3174; A., 1927, 143. Compare G. Charrier, *Atti R. Accad. Lincei*, 1927, [vi], 5, 889; A., 1064.

<sup>6</sup> See, for example, P. Uhlenhuth, P. Kuhn, and H. Schmidt, *Archiv f. Schiffs u. Tropen-Hygiene*, 1925, 29, 623; W. G. Christiansen, *J. Amer. Chem. Soc.*, 1926, 48, 1365; A., 1926, 722; W. C. Harden and F. Dunning, *ibid.*, 1927, 49, 1017; A., 544; C. H. Browning and others, *Proc. Roy. Soc.*, 1927, [B], 102, 1; A., 855.

<sup>7</sup> *Annalen*, 1925, 446, 148; A., 1926, 312. Compare A. F. Holleman, *Rec. trav. chim.*, 1923, 42, 355; A., 1923, i, 664.

nitrobenzene the three possible monomercurated products are formed in the ratio  $5:4:1 = o:m:p$ , and this has been confirmed by J. Jürgens.<sup>8</sup> The anomalous character of mercuration in similar cases is supported by the results of work on toluene<sup>9</sup> ( $43:13:44 = o:m:p$ ) and the three nitrotoluenes.<sup>10</sup> On the other hand, when a hydroxyl group is present as a substituent, it not only facilitates mercuration, but also appears to exert the principal orienting influence even when other substituents are present. Mercuration then appears to take place in *o*- and *p*-positions, if both are free, producing two monomercuri-derivatives, but there is a great tendency to form dimercuri-derivatives by substitution in both positions at once. There is a fair amount of evidence that the *o*- is preferred to the *p*-position.<sup>11</sup> This facilitating and directing influence of hydroxyl is apparently unaffected by the simultaneous presence of a nitro-, alkyl or aldehyde group or of either of the first two with the third.<sup>12</sup> So far no evidence of mercuration in the *m*-position in phenolic substances has been recorded, but it is admittedly difficult in these cases to isolate small quantities of such substances from the complex reaction mixtures formed.

Investigation of the mercuration of aniline and its derivatives and homologues, so far as it has gone, indicates that the amino-group behaves like the hydroxyl group with the possible exception that there is a greater tendency to favour the *p*- instead of the *o*-position,<sup>13</sup> but *o*-toluidine appears to behave exceptionally, since it is stated to yield only a dimercuri-derivative, which is neither 3:5- nor 4:6-.<sup>14</sup> The acetyl derivatives of aniline and its homologues exhibit the peculiarity that they may take up 3, 4, or even 5 acetoxymercuri-residues, producing eventually colloidal solutions the components of which do not react completely or simply with the agents usually used for determination of orientation.<sup>15</sup>

<sup>8</sup> *Rec. trav. chim.*, 1926, **45**, 61; **A.**, 1926, 312.

<sup>9</sup> S. Coffey, *J.*, 1925, **127**, 1029.

<sup>10</sup> *Idem*, *J.*, 1926, 637, 3215; **A.**, 1926, 629; 1927, 165; H. Burton, F. Hammond, and J. Kenner, *J.*, 1926, 1802; **A.**, 1926, 966.

<sup>11</sup> E. Mameli, *Gazzetta*, 1922, **52**, i, 352; ii, 1, 18, 23, 113; 1926, **56**, 948; **A.**, 1922, i, 695, 1080, 1082, 1083; **A.**, 1927, 268.

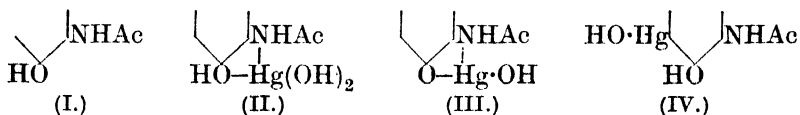
<sup>12</sup> T. A. Henry and T. M. Sharp, *J.*, 1922, **121**, 1055; 1924, **125**, 1049; 1926, 2432; **A.**, 1926, 1162.

<sup>13</sup> L. Vecchiotti, *Gazzetta*, 1914, **44**, 34; 1918, **48**, 78; 1921, **51**, 208; 1924, **54**, 411; 1927, **57**, 485; [with A. Michetti] 1925, **55**, 372; [with N. Carani] 1926, **56**, 147, 216; **A.**, 1914, i, 1063; 1919, i, 103; 1921, i, 902; 1924, i, 957; 1925, i, 1058; **A.**, 1926, 747, 852; 1927, 1098; G. Rossi and B. Cecchetti, *ibid.*, 1925, **55**, 869; **A.**, 1926, 312.

<sup>14</sup> L. Vecchiotti, *Gazzetta*, 1926, **56**, 155; **A.**, 1926, 747.

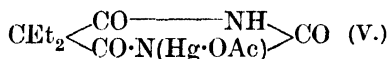
<sup>15</sup> G. Rossi and C. Bocchi, *ibid.*, 1925, **55**, 93; **A.**, 1925, i, 601; A. Bernardi, *ibid.*, 1926, **56**, 337; **A.**, 1926, 966.

There has been much speculation as to the mechanism by which mercuration is effected, one view being that in the mercuration of phenol or aniline an addition compound with mercuric acetate is first formed, the acetoxymercuri-residue then migrating to the contiguous carbon atom, but a careful investigation, by the freezing-point method, of the three components, solvent, mercuric acetate, and phenol, taken two at a time, and of the ternary system provided no evidence of the formation of such substances.<sup>16</sup> In the case of *o*-acetamidophenols, however, it has been found possible to isolate intermediate compounds, which indicate that the course of the reaction may be represented by the following partial formulæ.

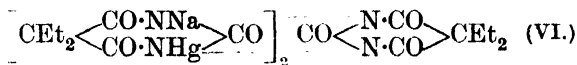


In the mercuration of sodium 3-acetamido-4-hydroxybenzoate, compounds represented by formulæ (II), (III), and (IV) have been isolated, (II) changing rapidly into (III), and the latter slowly into (IV), which alone has a mercury residue readily replaceable by iodine.<sup>17</sup>

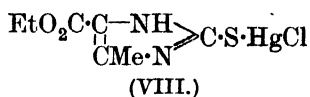
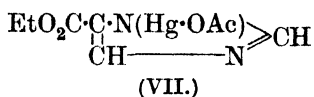
Several papers have appeared on the mercuration of pyrroles,<sup>18</sup> barbituric acid derivatives,<sup>19</sup> and other heterocyclic compounds. According to E. Rupp and K. Müller,<sup>19</sup> sodium diethylbarbiturate gives two mercury derivatives (V and VI), (VI) being produced



by dissolving, in dilute sodium hydroxide solution, the mercuri-hydroxy-derivative corresponding to (V), and allowing it to react



with more of the organic reagent. I. E. Balaban and H. King<sup>20</sup> have prepared two mercury compounds of substituted glyoxalines (VII and VIII) by treating, in alcoholic solution, ethyl glyoxaline-



<sup>16</sup> E. Mameli and G. Cocconi, *Gazzetta*, 1922, **52**, 113; *A.*, 1922, i, 1083.

<sup>17</sup> E. Maschmann, *Annalen*, 1926, **450**, 85, 98; *A.*, 1926, 1265; *Ber.*, 1926, 59, [B], 213; *A.*, 1926, 418.

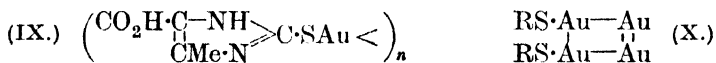
<sup>18</sup> G. Plancher and G. Rossi, *Gazzetta*, 1925, **55**, 61; *A.*, 1925, i, 601; H. Fischer and R. Müller, *Z. physiol. Chem.*, 1925, **148**, 155; *A.*, 1926, 75.

<sup>19</sup> P. Fleury, *Bull. Soc. chim.*, 1925, [iv], **37**, 1656; 1926, [iv], **39**, 99; *A.*, 1926, 305, 420; E. Rupp and K. Müller, *Arch. Pharm.*, 1926, **264**, 362; *A.*, 1926, 862.

<sup>20</sup> *J.*, 1927, 1858; *A.*, 977.

4(or 5)-carboxylate with mercuric acetate and ethyl 2-thiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylate with excess of mercuric chloride, respectively. The latter is stable to sodium hydroxide but not to ammonium sulphide or to hydrogen sulphide in presence of acids, whereas the former is decomposed by both reagents, and it is upon this difference in behaviour that the two positions of the mercury residues are assigned.

The same authors have also prepared 2-aurothiol-4(or 5)-methylglyoxaline-5(or 4)-carboxylic acid (IX) and its ethyl ester by the action of auric chloride on the thiol-acid and its ethyl ester respectively. These products are amorphous and give colloidal solutions,



and on that and other grounds are formulated as polymerides. The aurothiol acid so prepared always contains an excess of combined gold, due, the authors suggest, to the presence of such a product as (X), analogous in constitution with the polyarsenides formed when arsinic acids are over-reduced.

Numerous organic derivatives of other metals have been described, which cannot be referred to here, not because of any lack of appreciation of their interest and importance, especially in connexion with theories of co-ordination compounds, but solely for lack of space.

#### *Miscellaneous Alkaloids.*

During the last three years, the work on alkaloids dealt with in these Reports has been mainly synthetical, on known alkaloids and their derivatives, or on the proximate degradation products of alkaloids about whose nuclear structure something is known. There has accumulated during the period a considerable amount of work of a more pioneering character to which some reference may now be made.

*Aconitum Alkaloids.*—Part of the difficulty in dealing with the numerous and complex alkaloids now known to occur in various species of *Aconitum* is that of obtaining botanically authentic material in quantity, and special interest on that account attaches to the work on the alkaloids of various Japanese aconites of known botanical origin published by R. Majima and his collaborators.<sup>21</sup> It is suggested that in eight different species, seven alkaloids are present distinguished as japaconitines A, A<sub>1</sub>, A<sub>2</sub>, B, B<sub>1</sub>, C and C<sub>1</sub>, of which two, A and B, occur in all but one of the species examined,

<sup>21</sup> *Ber.*, 1924, **57**, [B], 1456, 1466, 1472; 1925, **58**, [B], 2047; *A.*, 1924, i, 1223, 1224, 1225; 1925, i, 1447; compare F. H. Carr, *J.*, 1912, **101**, 2241; G. Barger, *J.*, 1915, **107**, 231; O. L. Brady, *J.*, 1913, **103**, 1821.

this exception containing japaconitine  $A_2$  and Makoshi's jesaconatine, now shown to be acetylanisoyljesaconine,  $C_{35}H_{49}O_{12}N$ . Merck's aconitine, derived from *Aconitum Napellus*, is also divided into two aconitines, A and C, the aconine from the former being identical with the aconine from japaconitine  $A_2$ . There are therefore now nine "aconitines" of the formula  $(C_{34}H_{47}O_{11}N)$ , which are all acetylbenzoyl-"aconines" and in which only two of the "aconines" are identical. Moreover, seven of these "aconitines," viz., japaconitines A,  $A_1$ ,  $A_2$ , B,  $B_1$  and aconitines A and C, on oxidation all yield the same oxonitin, m. p.  $282^\circ$ ,  $[\alpha]_D - 41.9^\circ$ , and since in this product the acetyl and benzoyl groups are still intact, isomerism due to variation in position of one or both the acyl groups is excluded. Differences between the nine isomerides are based mainly on the solubilities and crystallising capacity of the hydrobromides, factors notoriously variable in alkaloids with the purity of the material, and the melting points and specific rotations of the nine bases as tabulated below suggest that reduction in the number may be possible by further work.

Japaconitines.				
	A.	$A_1$ .	$A_2$ .	B.
M. p. ....	202—203°	208—209°	199—201°	208—209°
$[\alpha]_D$ .....	+20.7°	+26.4°	+18.7°	+26.9°
				$B_1$ .
				194—195°
				+22°

Japaconitines.		Aconitines.	
	C.	$C_1$ .	A.
M. p. ....	195—196°	193—195°	202—203°
$[\alpha]_D$ .....	+18.3°	+23.2°	+18.1°
			C.
			203—204°
			+23.4°

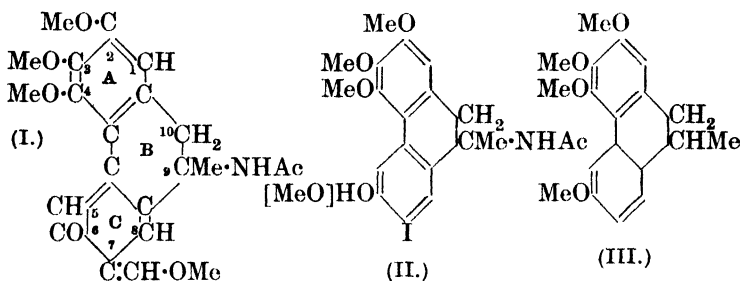
Further progress has been made in the examination of oxonitin, the formula of which seems now to be definitely established as  $C_{25}H_{33}O_{10}N$ , and this, from knowledge of the side chains present, can be extended to  $C_{13}H_{15}O_3(NH)(OMe)_3(C_6H_5\cdot CO\cdot O)(CH_3\cdot CO\cdot O)$ . On heating, oxonitin loses a molecule of acetic acid, giving pyroxonitin, which, in turn, on treatment with baryta in water-alcohol loses one molecule of benzoic acid, apparently without taking up a molecule of water as in an ordinary hydrolysis.

In the residual alkaloids of *A. Napellus* H. Schulze and G. Berger<sup>22</sup> were unable to find any picroaconitine (benzoylaconine), but isolated a new amorphous alkaloid, neopelline,  $C_{28}H_{33}O_5(OMe)_3(NMe).3H_2O$ , which on hydrolysis furnishes acetic and benzoic acids and a base, neoline,  $C_{23}H_{29}O_6N$ , also amorphous but giving a crystalline hydrobromide. According to the same authors, neopelline also occurs in *A. Stoeckianum*, Reich, along with an alkaloid provisionally

<sup>22</sup> *Arch. Pharm.*, 1924, 262, 553; *A.*, 1925, i, 283.

regarded as aconitine, since it only differs in a minute crystallographic detail from that base.<sup>23</sup>

*Colchicine*,  $C_{23}H_{25}O_6N$ .—This, the principal alkaloid of the autumn crocus, is the subject of two further papers by A. Windaus,<sup>24</sup> in which a considerable modification of his provisional formula is proposed, which represents the alkaloid as an interesting variant of what has been called the phenanthrene group of alkaloids (p. 173), although in these an *isoquinoline* group is present as in typical members of the group, or potentially present, as in the morphine section of the group. On heating with dilute acids, colchicine (I)



suffers demethylation of the side chain at 7, producing colchiceine, which also occurs in the autumn crocus, and itself on treatment with stronger acid undergoes deacetylation of the side chain at 9, forming trimethylcolchicinic acid. The latter yields diacyl derivatives which exist in *cis*- and *trans*-forms, due to acylation of the side chain :CH·OH at position 7, since both forms yield the same *N*-acyltrimethylcolchicinic acid on partial hydrolysis.

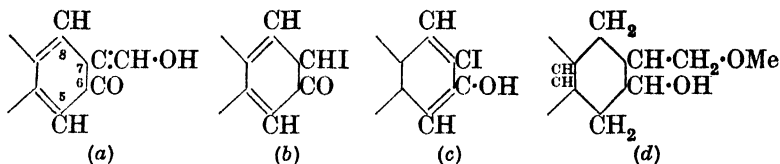
Colchiceine on treatment with iodine in potassium iodide solution yields iodo-*N*-acetylcolchicinol (II), which differs from colchiceine empirically by loss of ·CHO and gain of I, and behaves as an iodophenol. This reaction recalls the conversion of  $\beta$ -naphthol- $\alpha$ -aldehyde by the same means into  $\alpha$ -iodo- $\beta$ -naphthol,<sup>25</sup> with the difference that no aldehyde group can be traced in colchiceine, which, moreover, is readily convertible into its enolic methyl ether, colchicine. It is suggested, therefore, that this reaction takes place in ring C (formula I) as represented by the following partial formulæ (a), (b), (c).

<sup>23</sup> *Arch. Pharm.*, 1927, **265**, 524; *A.*, 1097.

<sup>24</sup> *Annalen*, 1924, **439**, 59; *A.*, 1924, i, 1089; [with H. Schiele] *Nachr. K. Wiss. Göttingen*, 1923, 17; *A.*, 1924, i, 72. For previous work, see *Sitzungsber. Heidel. Akad. Wiss.*, 1910, 1; 1911, 1; 1914, 18; *A.*, 1911, i, 904; 1915, i, 708.

<sup>25</sup> A. Windaus and H. Schiele, *Ber.*, 1923, **56**, [B], 846; *A.*, 1923, i, 580.





The methyl ether of iodo-*N*-acetylcolchinel (II) on further oxidation furnishes a product which is regarded as 5(?)-iodo-4-methoxyphthalic acid, since on reduction it produces 4-methoxyphthalic acid, and this work with the evidence given above is regarded as establishing the existence of ring C (formula I) and the location in it of groups :CH·OMe and CO at positions 7 and 6 or 6 and 7, respectively. On catalytic hydrogenation, both colchicine and colchicine take up eight atoms of hydrogen; these are believed to be entirely absorbed by the components of ring C (formula I), which is thereby changed to that shown by partial formula (d).

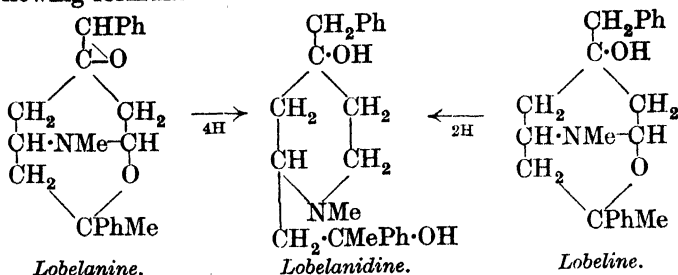
The positions of the side chains of ring B (formula I) are fixed by the facts (1) that *N*-acetylcolchinel methyl ether, formed by reduction of the methyl ether of iodo-*N*-acetylcolchinel (II), is oxidised by chromic acid to 4-methoxy-*o*-phthalimide, whence the nitrogen atom must be attached to the carbon atom (9 in formula I) *ortho* to the junction with ring C; (2) the formation of terephthalic and mellitic acids together with other products when colchicine is fused with potassium hydroxide and the resulting demethylated and deaminated substance is oxidised with permanganate; and (3) the production of a carbonyl compound when colchicine is oxidised to oxycolchicine [conversion of :CH<sub>2</sub> at 10, formula (I), to :CO].

Evidence of a phenanthrene nucleus is provided by the formation of a tetramethoxymethyldihydrophenanthrene (III) when colchinel methyl ether, made by obvious methods from *N*-acetylcolchinel (II), is "exhaustively methylated," the nitrogen being eliminated as trimethylamine.

*Lobeline and Allied Alkaloids*.—H. Wieland<sup>26</sup> and his collaborators have shown that the lobelia plant (*Lobelia inflata*) contains the following five alkaloids: lobeline, C<sub>22</sub>H<sub>27</sub>O<sub>2</sub>N, lobelidine, C<sub>20</sub>H<sub>25</sub>O<sub>2</sub>N, lobelanine, C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>N, lobelanidine, C<sub>22</sub>H<sub>29</sub>O<sub>2</sub>N, and isolobelanine, C<sub>22</sub>H<sub>25</sub>O<sub>2</sub>N. Three of these are closely related, lobeline and lobelanine being convertible into lobelanidine by reduction with sodium amalgam in acetic acid, two and four atoms of hydrogen being added respectively. These reductions represent

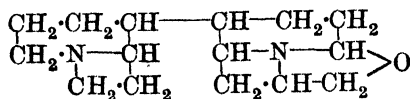
<sup>26</sup> H. Wieland, *Ber.*, 1921, **54**, [B], 1784; [with C. Schöpf and W. Hermesen] *Annalen*, 1925, **444**, 40; C. Schöpf and E. Boettcher, *ibid.*, 1926, **448**, 1; *A.*, 1921, i, 802; 1925, i, 1087; *A.*, 1926, 744.

the conversion of ether linkages into hydroxyl groups as shown in the following formulæ :



The presence of two unsubstituted benzene rings is proved by the formation of two molecules of benzoic acid when lobelanine is oxidised by potassium permanganate, and the existence of a potential third benzene ring is suggested by the formation of acetophenone, methylamine and fluorene when lobelanine is heated with dilute hydrochloric acid, and of the corresponding substances, phenyl-methylcarbinol, methylamine, and benzhydrol, when the same alkaloid is heated with alcoholic potassium hydroxide. Of the various formulæ which will adequately explain these reactions and are discussed in the original, choice of the three given above is made from the fact that lobelanidine is stable to permanganate and that lobelane,  $\text{C}_{22}\text{H}_{26}\text{N}$ , produced by the reduction of the dichloride of lobelanidine does not undergo the usual Hofmann degradation.

*Lupin Alkaloids.*—Of the four alkaloids obtained from *Lupinus* spp., a constitution has been assigned only to one, sparteine (lupinidine). A fifth base, spathulatine,  $\text{C}_{33}\text{H}_{64}\text{O}_5\text{N}_4$ , was added by J. F. Crouch,<sup>27</sup> who also recorded the presence of the known alkaloid *d*-lupanine in *Lupinus Kingsii*.<sup>28</sup> The latter base has been investigated by H. Thoms and K. Bergershoff,<sup>29</sup> who confirm other workers' experience of its low reactivity, but assign the following constitution to it on the rather meagre evidence it has so far been possible to obtain :



*Minor Alkaloids.*—E. Späth and W. Stroh<sup>30</sup> have shown that the formula of calycanthine must be increased to  $\text{C}_{22}\text{H}_{28}\text{N}_4$  and have with some difficulty prepared a dimethiodide from it.

<sup>27</sup> *J. Amer. Chem. Soc.*, 1924, **46**, 2807; *A.*, 1925, i, 61.

<sup>28</sup> *Ibid.*, 1925, **47**, 2584; *A.*, 1925, i, 1447.

<sup>29</sup> *Arch. Pharm.*, 1925, **263**, 3; *A.*, 1925, i, 575.

<sup>30</sup> *Ber.*, 1925, **58**, [B], 2131; *A.*, 1925, i, 1447.

J. L. Simonsen<sup>31</sup> has shown that conessine dimethiodide,  $C_{24}H_{40}N_2 \cdot 2MeI$ , on treatment with silver hydroxide, yields apoconessine,  $C_{22}H_{33}N$ , which in turn furnishes a methiodide, m. p. 283—285°. Similarly, conessine dimethosulphate, when heated with aqueous potassium hydroxide, furnishes a hygroscopic base,  $C_{26}H_{44}N_2$ , from which a crystalline dimethiodide can be obtained.

O. Keller, who has already published a series of papers on the alkaloids of the *Ranunculaceæ*, has re-investigated those of staves-acre seeds, *Delphinium Staphisagria*,<sup>32</sup> with results that may be regarded as promising for further additions to knowledge of this little-known group of alkaloids the phytological and pharmacological relationships of which indicate a close connexion with the aconitines.

Vasicine,  $C_{11}H_{12}ON_2$ , found in the Indian plant *Adhatoda vasica*, has been characterised more fully and shown to be oxidised by potassium permanganate to 4-hydroxyquinazoline,<sup>33</sup> whence it is regarded as probably a 2-propyl-(or isopropyl)-4-hydroxyquinazoline, a particularly interesting simple alkaloidal nucleus.

From akuamma seed, *Picralima klaineana*, Pierre, a West African fever remedy, a series of four alkaloids has been isolated. Two of these are amorphous and two crystalline, only one of which, akuammine,  $C_{22}H_{28}O_4N_2$ , is regularly present in quantity. It contains a methylimino-, a methoxyl, and a hydroxyl group, and the two remaining oxygen atoms may be present in the form of a lactone group, as the alkaloid is hydrated by alkali to a substance,  $C_{22}H_{30}O_5N_2$ , of which the methyl ester appears to be formed when akuammine is treated with methyl iodide in presence of alkali.<sup>34</sup>

Echitamine,  $C_{22}H_{28}O_4N_2$ , first isolated by Hesse in 1880, has been re-examined and several obscure points in its chemistry have been cleared up by the observation that it is the readily hydrolysed methyl ester of demethylechitamine,  $C_{21}H_{26}O_4N_2$ . From what is known of the functions of the oxygen and nitrogen atoms, the empirical formula of the latter may be extended to either

$C_{19}H_{20}O(NMe)(NH)(OH) \cdot CO_2H$  or  $C_{19}H_{20}N(NMe)(OH)_2 \cdot CO_2H$ , it being still uncertain whether in the diacetyl derivative the second acetyl group replaces H in NH or OH, although the latter is the more probable. On distillation with alkali, echitamine furnishes

<sup>31</sup> J., 1926, 2123; A., 1926, 1047. See also S. Osada, J. Pharm. Soc. Japan, 1927, 98.

<sup>32</sup> Arch. Pharm., 1925, 263, 274; A., 1925, i, 830.

<sup>33</sup> J. N. Sen and T. P. Ghose, J. Indian Chem. Soc., 1925, 1, 315; A., 1925, i, 958; T. P. Ghose, *ibid.*, 1927, 4, 1; A., 785.

<sup>34</sup> T. A. Henry and T. M. Sharp, J., 1927, 1950; A., 982; compare Cliniquart, Bull. Acad. roy. med. Belg., 1926, 492; J. Pharm. Belg., 1927, 9, 187.

methylamine and two other bases, one of which is probably an indole derivative.<sup>35</sup>

Much activity has also been shown in the examination of the alkaloids of *Ephedra*, spp., perhaps the most interesting point being the isolation of a third base, *l*-methylephedrine, from the Chinese drug Ma Huang<sup>36</sup> (*Ephedra sinica*, Stapf.). A considerable number of papers on the alkaloids of yohimbehe and quebracho have appeared, but as this subject is attracting the attention of a number of investigators, a review of the work may reasonably be postponed until some of the present confusion in details has been cleared up. It is perhaps also worth mentioning that two alkaloids, "yageine"<sup>37</sup> and "telepathine," the mysterious character of which is indicated by the second name, have been found to be identical and to consist of the well-known alkaloid harmine<sup>38</sup> (see p. 160).

T. A. HENRY.

<sup>35</sup> J. A. Goodson and T. A. Henry, *J.*, 1925, **127**, 1640; *A.*, 1925, i, 1166.

<sup>36</sup> S. Smith, *ibid.*, 1927, 2056; **A.**, 1094.

<sup>37</sup> A. M. Barriga Villalba, *J. Soc. Chem. Ind.*, 1925, **44**, 205; *A.*, 1925, i, 828.

<sup>38</sup> Private communication from Dr. Guggenheim of Basle. This work is reviewed in the *Annual Reports on Applied Chemistry*, 1927, **12**.

## ANALYTICAL CHEMISTRY.

DURING the period under review many delicate tests for the elements and radicals have been examined and described. It is satisfactory to record progress in devising specific reactions which may be applied to detect single elements or to group certain elements analytically. Two trustworthy tests for aluminium have come under notice. The use of dyes as indicators for the determination of halogens has been extensively investigated; the procedure consists in the adsorption of the dye on the silver halide, the slightest excess of silver producing a distinctively coloured silver salt of the dye which is more soluble than the precipitated halide.

In general volumetric determinations the question of accurate standard substances has been inquired into. A fair range of definite standard materials is thus becoming available for various volumetric processes. Particular attention may be directed to the value of the method of precipitation and determination of certain metals by means of 8-hydroxyquinoline ("oxine"). Five metals constitute a "hydroxyquinoline" group, since they may be precipitated from tartrate solutions in which caustic soda is also present. One advantage of this process of determining certain metals is that the "factor" for calculation of the metal from the weight of precipitate is small, so that a comparatively large weight of precipitate is obtained from very small proportions of metal.

The troublesome separation of aluminium from beryllium has been advanced definitely by a "tannin" method of separation.

A thorough investigation of the possible sources of error in organic analysis has been carried out, showing the kind of error which may be anticipated in normal working. At the same time one of the difficulties in the ter Meulen process of determining nitrogen has been dealt with. Some attention has likewise been directed to the more accurate determination of elements such as arsenic, phosphorus, and selenium in organic compounds.

Potentiometric methods have been studied, more particularly with reference to the determination of the end-points in titrations, and one simplified method has come under observation.

### *Inorganic Analysis.*

*Qualitative.*—Further work on the qualitative detection of metals in single drops of the solution to be tested has resulted <sup>1</sup> in a rapid

<sup>1</sup> N. A. Tananiev, *J. Russ. Phys. Chem. Soc.*, 1926, 58, 219; *A.*, 1927, 223.

scheme for the detection of metals which give colour reactions in the presence of one another. A detailed method of qualitative analysis avoiding the use of hydrogen sulphide, thioacetic acid, and sulphides has been presented.<sup>2</sup> When salts of each of 32 elements are mixed with cobalt, nickel, or chromium nitrates, and a strip of filter-paper is immersed in the mixed solution, then dried and burnt, distinctive colorations are obtained; this method is preferred to the ordinary blowpipe test on charcoal.<sup>3</sup>

Photomicrographs of the characteristic double bromides of cadmium with brucine and with quinine are given,<sup>4</sup> and also of the complex copper zinc and cadmium zinc mercurithiocyanates.<sup>5</sup> The formation of a blue coloration or precipitate with potassium cobaltothiocyanate serves, in the absence of copper and lead, as a delicate test for mercury; <sup>6</sup> the presence of bismuth may cause the precipitate to be violet in colour. Hot dilute solutions of bismuth nitrate or chloride give on addition of dimethylglyoxime and ammonia an intense yellow coloration or precipitate; <sup>7</sup> arsenic, antimony, zinc, cobalt, manganese, and ferric salts interfere with the reaction. Bismuth salts in nitric acid solution give with potassium cobalticyanide a characteristic crystalline precipitate which is not darkened with 10% potash solution (distinction from silver and mercurous cobalticyanides) but is darkened by alkaline stannite solution (distinction from cadmium and zinc).<sup>8</sup> Addition of a solution of antimony pentachloride in hydrochloric acid to a dye of the xanthone group, e.g., tetraethylrhodamine, produces a violet to blue fluorescence or colour; <sup>9</sup> molybdenum, bismuth, thallic, gold, and mercuric salts and colloidal tungstic acid give similar reactions.

The purple or pink coloration given with iron salts, in the absence of oxidising agents, by thioglycollic acid followed by ammonia probably depends on the formation of a coloured ferrous thioglycollic complex ion; sufficient reagent must be added to reduce any ferric iron present.<sup>10</sup> The method may be applied quantitatively and its delicacy is not affected by the presence of most other salts. When disodium hydrogen phosphate is added gradually with intermittent shaking to a neutral ferrous solution floating on a

<sup>2</sup> O. Macchia, *Notiz. chim.-ind.*, 1927, 2, 191; *A.*, 1045; *Z. anal. Chem.*, 1927, 72, 201.

<sup>3</sup> D. Migliacci and C. Crapetta, *Ann. Chim. Appl.*, 1927, 17, 66; *A.*, 329.

<sup>4</sup> A. Martini, *Anal. Asoc. Quím. Argentina*, 1927, 15, 52; *A.*, 953.

<sup>5</sup> R. Montequi, *Anal. Fis. Quím.*, 1927, 25, 52; *A.*, 436.

<sup>6</sup> B. Ormont, *Z. anal. Chem.*, 1927, 70, 308; *A.*, 325; *Z. anorg. Chem.*, 1927, 161, 337; *A.*, 531.

<sup>7</sup> H. Kubina and J. Plichta, *Z. anal. Chem.*, 1927, 72, 11; *A.*, 1048.

<sup>8</sup> A. Benedetti-Pichler, *ibid.*, 1927, 70, 257; *A.*, 331.

<sup>9</sup> E. Eegriwe, *ibid.*, p. 400; *A.*, 437.

<sup>10</sup> E. Lyons, *J. Amer. Chem. Soc.*, 1927, 49, 1916; *A.*, 953.

chloroform solution of oximinoacetophenone, a blue coloration develops in the chloroform layer;<sup>11</sup> cobalt, nickel, manganese, copper, zinc, cadmium, lead, and mercury impart colorations to the chloroform ranging from yellow to brown. 1:2:5:8-Tetrahydroxyanthraquinone gives with aluminium compounds in faintly acid solution an intense violet coloration which may be utilised for the determination of small quantities of the metal;<sup>12</sup> tin, antimony, and bismuth are rendered inactive by addition of sodium tartrate, but copper and iron must be removed. The formation of a pink lake with alizarin serves as a confirmatory test for aluminium.<sup>13</sup>

The best method for the micro-detection of zinc by precipitation as cobalticyanide followed by conversion into Rinman's green has been described, but a preliminary separation from other metals of the ammonium sulphide group is generally necessary.<sup>8</sup> The presence of zinc is indicated by a turbidity when diphenylamine or diphenylbenzidine acetate is added to the solution (acidified with acetic acid) followed by potassium ferricyanide;<sup>14</sup> small amounts of chromate do not influence the test. When added to a strongly ammoniacal cobalt solution, sodium hyposulphite produces a yellow, orange, ruby-red, or dark red coloration, or a brownish-black precipitate, according to the concentration of the cobalt.<sup>15</sup>

Magnesium may be detected by the red coloration developed in alkaline solution by addition of titan-yellow;<sup>16</sup> calcium and barium increase the intensity of the colour, whilst aluminium, tin, and bismuth interfere. The reaction has been applied to the colorimetric determination of traces of magnesium,<sup>17</sup> and also to the detection of magnesium in plant tissue.<sup>18</sup> Zinc uranyl acetate gives with neutral but not too dilute solutions containing sodium a yellow crystalline precipitate of a triple acetate.<sup>19</sup> For the microchemical detection of beryllium the formation of uranyl sodium beryllium acetate (analogous to the zinc salt just mentioned) and of beryllium acetylacetonate are recommended.<sup>20</sup> The formation of molybdenum thiocyanate is utilised for the qualitative detection of this metal.<sup>21</sup>

<sup>11</sup> F. Kröhnke, *Ber.*, 1927, **60**, [B], 527; **A.**, 332.

<sup>12</sup> I. M. Kolthoff, *Chem. Weekblad*, 1927, **24**, 447; **A.**, 1047.

<sup>13</sup> W. J. Allardyce, *J. Amer. Chem. Soc.*, 1927, **49**, 1991; **A.**, 953.

<sup>14</sup> W. H. Cone and L. C. Cady, *ibid.*, p. 2214; **A.**, 1046.

<sup>15</sup> P. Falciola, *Giorn. Chim. Ind. Appl.*, 1926, **8**, 612; **A.**, 1927, 333.

<sup>16</sup> I. M. Kolthoff, *Chem. Weekblad*, 1927, **24**, 254; **A.**, 639.

<sup>17</sup> *Idem*, *Biochem. Z.*, 1927, **185**, 344; **A.**, 847.

<sup>18</sup> H. Eilers, *Chem. Weekblad*, 1927, **24**, 448; **A.**, 1046.

<sup>19</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1927, **70**, 397; **A.**, 436.

<sup>20</sup> V. Caglioti, *Rend. Accad. Sci. fis. mat. Napoli*, 1927, [iii], **33**, 177; **A.**, 1046.

<sup>21</sup> F. C. Krauskopf and C. E. Swartz, *J. Amer. Chem. Soc.*, 1926, **48**, 3021; **A.**, 1927, 127.

The presence of traces of the platinum metals in silver beads obtained by cupellation causes peculiarities in the surface crystallisation which permit of the identification of the foreign metal.<sup>22</sup> The reaction between aurintricarboxylic acid ("aluminon") and the hydroxides of scandium, gallium, indium, thallium, and germanium has been investigated.<sup>23</sup>

The coloration given with safranin-T in the presence of mineral acid serves to detect one part of nitrite in 5,000,000 parts of water; nitrates are detected after reduction to nitrite with magnesium and dilute sulphuric acid.<sup>24</sup> Examination of the reaction of a large number of dyes with nitrous acid followed by a coupling agent shows that magenta is the most sensitive, especially when used in conjunction with an  $\alpha$ -derivative such as  $\alpha$ -naphthol,  $\alpha$ -naphthylamine, or H-acid rather than  $\beta$ -naphthol.<sup>25</sup> A dichroic solution results when a nitrate, even in small quantities, is mixed with sodium nitrite and added to a solution of *o*-cresol in concentrated hydrochloric acid.<sup>26</sup> Nitrates, after removal of halides, give a red coloration with a solution of diaminophenol in sulphuric acid; some other oxidising agents which give the test, unlike nitrates however, afford a similar coloration with a solution of the reagent in hydrochloric acid.<sup>27</sup>

The sensitivity of the test for sulphites with fast-blue R is about 1 in 175,000; <sup>24</sup> thiosulphates and thionates do not give the reaction, and sulphides and hydroxides interfere. The sensitiveness of some reagents and test papers for gaseous hydrogen sulphide<sup>28</sup> and gaseous phosphine<sup>29</sup> has been examined. Reaction with nitroprusside solution in the presence of hydrogen sulphide serves to distinguish between normal, mono-, and di-hydrogen salts of orthophosphoric acid.<sup>30</sup> Minute traces of selenium in hydrochloric acid give with thiocarbamide a red colour; with larger quantities, the element separates out quantitatively.<sup>31</sup>

Methods for the identification of iodides and bromides, alone or together, have been examined,<sup>32</sup> and also the micro-reactions of

<sup>22</sup> C. O. Bannister, *J. Roy. Micros. Soc.*, 1927, **47**, 143; **A.**, 746.

<sup>23</sup> R. B. Corey and H. W. Rogers, *J. Amer. Chem. Soc.*, 1927, **49**, 216; **A.**, 1219.

<sup>24</sup> E. Eegriwe, *Z. anal. Chem.*, 1926, **69**, 382; **A.**, 1927, 125.

<sup>25</sup> J. V. Dubský and A. Okáč, *Rec. trav. chim.*, 1927, **46**, 296; **A.**, 688.

<sup>26</sup> A. H. Ware, *Analyst*, 1927, **52**, 332; **A.**, 638.

<sup>27</sup> D. Buznea and R. Cernatesco, *Ann. sci. Univ. Jassy*, 1927, **14**, 302; **A.**, 534.

<sup>28</sup> M. Wilmet, *Compt. rend.*, 1927, **184**, 287; **A.**, 221.

<sup>29</sup> *Idem*, *ibid.*, p. 1456; **A.**, 744.

<sup>30</sup> L. Rossi, *Anal. Asoc. Quím. Argentina*, 1926, **14**, 239; **A.**, 1927, 125.

<sup>31</sup> P. Falcicola, *Ann. Chim. Appl.*, 1927, **17**, 357; **A.**, 952.

<sup>32</sup> J. von Mikó, *Arch. Pharm.*, 1927, **265**, 445; **A.**, 744.



chlorides, bromides, and iodides.<sup>33</sup> A method for the oxidation of cyanides, thiocyanates, sulphides, sulphites, thiosulphates, ferro- and ferri-cyanides by hydrogen peroxide prior to the detection of chlorides is described.<sup>34</sup>

The application of zirconium salts for the removal of phosphates in qualitative analysis has been further examined.<sup>35</sup>

*Quantitative.*—Considerable attention has been devoted during the year to the subject of standard substances for volumetric solutions. Improvements have been made in the method of using potassium permanganate as an acidimetric standard.<sup>36</sup> Other compounds investigated are borax,<sup>37</sup> oxalic acid dihydrate and potassium quadroxalate,<sup>38</sup> yellow mercuric oxide,<sup>39</sup> potassium hydrogen tartrate,<sup>40</sup> and potassium hydrogen carbonate.<sup>41</sup> Mercury, which can be obtained readily in the pure state, forms a useful standard for thiocyanate solutions instead of silver.<sup>39</sup> Iron suitable for the standardisation of permanganate is prepared by the electrolysis of a solution of pure ferrous chloride containing sodium chloride and boric acid, but iron deposited from oxalate solutions invariably contains carbon.<sup>42</sup> For the preservation of thiosulphate solutions, the addition of borax, disodium hydrogen phosphate, or carbon disulphide is advised.<sup>43</sup> Solutions of oxalic acid should be preserved in the dark.<sup>44</sup>

Some of the methoxytriphenylcarbinols have been examined with reference to their use as one-colour indicators.<sup>45</sup>

The addition of small quantities of starch, preferably alkaline, brings about the flocculation of many troublesome precipitates encountered in analysis.<sup>46</sup> A general study of the conditions for producing coalescence of precipitates has also been made.<sup>47</sup>

Anhydrous barium or mixed alkaline-earth perchlorates have been examined as dehydrating agents.<sup>48</sup> Mixed ammonium sulphate

<sup>33</sup> E. M. Chamot and C. W. Mason, *Mikrochem.*, 1927, **5**, 85; **A.**, 744.

<sup>34</sup> (Mlle.) E. Spirescu, *Bul. Soc. chim. România*, 1926, **8**, 115; **A.**, 1927, 637.

<sup>35</sup> F. Oberhauser, *Ber.*, 1927, **60**, [B], 36; **A.**, 222.

<sup>36</sup> T. Heczko, *Z. anal. Chem.*, 1927, **71**, 332; **A.**, 848.

<sup>37</sup> T. Milobedski and H. Kaminska, *Bull. Soc. chim.*, 1927, [iv], **41**, 957; **A.**, 846.

<sup>38</sup> K. O. Schmitt, *Z. anal. Chem.*, 1927, **71**, 273; **A.**, 845.

<sup>39</sup> I. M. Kolthoff and L. H. van Berk, *ibid.*, p. 339; **A.**, 845.

<sup>40</sup> G. Favrel, *Ann. Chim. anal.*, 1927, [ii], **9**, 161; **A.**, 743.

<sup>41</sup> K. O. Schmitt, *Z. anal. Chem.*, 1927, **70**, 321; **A.**, 433.

<sup>42</sup> L. Moser and W. Schöninger, *ibid.*, p. 235; **A.**, 332.

<sup>43</sup> I. Yoshida, *J. Chem. Soc. Japan*, 1927, **48**, 26; **A.**, 435.

<sup>44</sup> S. Ishimaru, *Bull. Chem. Soc. Japan*, 1927, **2**, 134; **A.**, 743.

<sup>45</sup> I. M. Kolthoff, *J. Amer. Chem. Soc.*, 1927, **49**, 1218; **A.**, 637.

<sup>46</sup> W. Clayton, *Analyst*, 1927, **52**, 76; **A.**, 329.

<sup>47</sup> H. M. Trimble, *J. Physical Chem.*, 1927, **31**, 601; **A.**, 435.

<sup>48</sup> G. F. Smith, *Ind. Eng. Chem.*, 1927, **19**, 411; **A.**, 438.

and halide may be used for converting some of the salts of a number of metals into the sulphates.<sup>49</sup> A number of examples of induced precipitation of sulphides is given.<sup>50</sup>

The application of 8-hydroxyquinoline ("oxine") as an analytical reagent has been examined in considerable detail. The salts of the type  $C_9H_6N \cdot OM^I$ , which are readily formed with most common metals, are generally insoluble in dilute acetic acid and in ammoniacal tartrate solution; in caustic soda solution containing tartrate only copper, zinc, cadmium, magnesium, and ferrous iron are precipitated—these metals constitute the "hydroxyquinoline group."<sup>51</sup> The salts are crystalline, easily filtered and washed, and may be used conveniently for the determination of metals; the precipitates may be weighed directly or the hydroxyquinoline residue determined volumetrically by means of standard bromide-bromate solution.<sup>52</sup> The complexes are fairly stable to heat, and may be quantitatively decomposed by careful ignition in the presence of anhydrous oxalic acid, the metal being then weighed as oxide. It is known that neutral salts of magnesium, zinc, aluminium, and copper cannot be titrated directly with alkali hydroxides on account of the formation of basic salts and of adsorption of alkali; these errors are completely eliminated by addition of "oxine" to precipitate the metals, the liberated acid being then neutralised with standard alkali with phenol-red or naphtholphthalein as indicator.<sup>53</sup> Further references are made below in connexion with the individual metals so far investigated. The use of this reagent permits of a great saving of time in many practical determinations, as, for example, that of magnesium in aluminium alloys.

Silver may be separated from lead by treating the mixed oxalates with a small excess of ammonia, whereby silver oxalate is dissolved.<sup>54</sup> Under no modification of conditions could quantitative conversion of lead to peroxide by persulphate in ammoniacal or sodium hydroxide solution be obtained.<sup>55</sup> An investigation of the solubility of lead sulphate in water and in solutions of electrolytes, with the view of ascertaining the most favourable conditions for the gravimetric determination of lead as sulphate, indicates that the final concentration of sulphuric acid should be about 0.3%.<sup>56</sup>

<sup>49</sup> L. Moser and W. Maxymowicz, *Ber.*, 1927, **60**, [B], 646; **A.**, 435.

<sup>50</sup> W. Böttger and K. Druschke, *Annalen*, 1927, **453**, 315; **A.**, 536.

<sup>51</sup> R. Berg, *J. pr. Chem.*, 1927, [ii], **115**, 178; **A.**, 674.

<sup>52</sup> *Idem*, *Pharm. Ztg.*, 1926, **71**, 1542.

<sup>53</sup> F. L. Hahn and E. Hartleb, *Z. anal. Chem.*, 1927, **71**, 225; **A.**, 745.

<sup>54</sup> H. Brintzinger, *ibid.*, 1927, **70**, 448; **A.**, 535.

<sup>55</sup> P. Ekwall, *ibid.*, p. 161; **A.**, 223.

<sup>56</sup> M. Huybrechts and H. Ramelot, *Bull. Soc. chim. Belg.*, 1927, **36**, 239; **A.**, 536.

Copper is precipitated by 8-hydroxyquinoline from dilute acetic acid or from sodium hydroxide-tartrate solution; in this latter case, ferric iron, bismuth, tin, arsenic, and antimony are not precipitated. The copper may be determined subsequently by the iodide method or, in the absence of other metals of the "oxine" group, the complex may be weighed directly.<sup>57</sup> Copper, after reduction to the cuprous condition, is separated from mercury as thiocyanate; excess of reagent in the filtrate is oxidised with bromine before precipitation of the mercury as sulphide.<sup>58</sup> Cupric salts are reduced by shaking with bismuth amalgam in warm hydrochloric acid solution; the cuprous chloride is then titrated with dichromate, diphenylamine being used as internal indicator.<sup>59</sup> Stannic salts are similarly reduced. For the rapid determination of copper, a process whereby copper pyridine thiocyanate may be weighed directly has been worked out.<sup>60</sup>

The precipitation of bismuth with pyrogallol has been applied to the micro-determination of this metal,<sup>61</sup> and a number of volumetric methods has also been investigated.<sup>62</sup> Bismuth can be separated from metals other than mercury, silver, lead, and thallium by addition of 8-hydroxyquinoline in slightly acid solution, followed by potassium iodide;<sup>63</sup> the precipitated salt  $(C_9H_7ON)_2HBI_4$  is titrated with potassium iodate solution. In the absence of halides, bismuth is precipitated in the usual way from acetic or ammoniacal tartrate solution by "oxine."<sup>64</sup>

Cadmium is precipitated from very dilute acetic acid or alkaline-tartrate solution by 8-hydroxyquinoline as the dihydrate. Dried at  $100^\circ$ , the precipitate consists of  $Cd(C_9H_6ON)_2 \cdot 1\frac{1}{2}H_2O$ , which becomes anhydrous at  $130^\circ$ . The cadmium compound is readily soluble in hot 10% acetic acid, the corresponding copper salt being precipitated under these conditions.<sup>64a</sup> The use of  $\beta$ -naphthaquinoline and potassium iodide allows the precipitation of cadmium from dilute sulphuric acid solution as the salt  $(C_{13}H_9N)_2H_2CdI_4$  in presence of zinc, cobalt, nickel, manganese, ferrous iron, chromium, aluminium, and magnesium;<sup>63</sup> if tin and antimony are present, large proportions of sodium tartrate or ammonium oxalate are necessary.

<sup>57</sup> R. Berg, *Z. anal. Chem.*, 1927, **70**, 341; **A.**, 436.

<sup>58</sup> J. Krauss, *Z. angew. Chem.*, 1927, **40**, 354; **A.**, 436.

<sup>59</sup> K. Someya, *Z. anorg. Chem.*, 1927, **160**, 404; **A.**, 332; *Sci. Rep. Tôhoku Imp. Univ.*, 1927, **16**, 515; **A.**, 848.

<sup>60</sup> G. Spacu and J. Dick, *Z. anal. Chem.*, 1927, **71**, 185; **A.**, 746.

<sup>61</sup> R. Strebing and E. Flaschner, *Mikrochem.*, 1927, **5**, 12; **A.**, 334.

<sup>62</sup> W. Strecker and A. Herrmann, *Z. anal. Chem.*, 1927, **72**, 5; **A.**, 1048.

<sup>63</sup> R. Berg and O. Wurm, *Ber.*, 1927, **60**, [B], 1664; **A.**, 847.

<sup>64</sup> R. Berg, *Z. anal. Chem.*, 1927, **72**, 177.

<sup>64a</sup> *Idem, ibid.*, 1927, **71**, 321; **A.**, 847.

Tin can be quantitatively separated from quinquevalent antimony, arsenic, lead, zinc, and certain other metals by precipitation with "cupferron."<sup>65</sup> Stannous chloride can be satisfactorily titrated with ferric chloride at the ordinary temperature if the solution contains at least half its volume of concentrated hydrochloric acid, indigo-carmin being used as internal indicator.<sup>66</sup> In the iodometric determination of the antimonious ion, addition of a large excess of potassium iodide and about 15% of hydrochloric acid inhibits the reverse reaction and gives good results rapidly.<sup>67</sup> Antimony can be separated from the alkali metals as, for example, in antimonates, by heating in a current of hydrogen chloride. Some observations on the bromate titration of antimony are described.<sup>68</sup>

For the reduction of chromic chloride, shaking with zinc amalgam in an atmosphere of carbon dioxide is recommended; the resulting chromous chloride is then titrated with permanganate, dichromate, or ferric chloride.<sup>69</sup> It is claimed that the use of "infusible white precipitate" for the precipitation of chromium prior to gravimetric determination as oxide gives more accurate results than the usual method using ammonia;<sup>70</sup> the application of this reagent to the determination of iron, aluminium, and chromium is also dealt with elsewhere.<sup>71</sup> The colorimetric determination of iron by means of salicylic acid can be used in the presence of metals of the first three groups, of sulphate, nitrate, acetate, moderate amounts of phosphate, and small quantities of organic matter; free alkali or organic polybasic acids destroy the colour.<sup>72</sup> Some observations on Knop's method of titrating iron are to be found in a paper on the determination of ferrous iron in silicates.<sup>73</sup> A procedure for the direct determination of small quantities of iron as the bis-*p*-chlorophenyl-phosphate has been described.<sup>74</sup>

A procedure for the separation of aluminium from iron, copper, and magnesium by means of "cupferron" has been described,<sup>75</sup>

<sup>65</sup> A. Pinkus and (Mlle.) J. Claessens, *Bull. Soc. chim. Belg.*, 1927, **36**, 413; **A.**, 848.

<sup>66</sup> W. Schluttig, *Z. anal. Chem.*, 1927, **70**, 55; **A.**, 223.

<sup>67</sup> A. Travers and Jouot, *Compt. rend.*, 1927, **184**, 605; **A.**, 334.

<sup>68</sup> G. Jander and W. Brüll, *Annalen*, 1927, **453**, 332; **A.**, 640.

<sup>69</sup> K. Someya, *Z. anorg. Chem.*, 1927, **160**, 355; **A.**, 333; *Sci. Rep. Tôhoku Imp. Univ.*, 1927, **16**, 397.

<sup>70</sup> W. Punm, *Collegium*, 1927, 202; **B.**, 480.

<sup>71</sup> M. Kranjčević and G. Rukonić, *Arhiv Hemiju*, 1927, **1**, 18; **A.**, 746.

<sup>72</sup> A. Sagaidatchni and M. Ravitch, *J. Russ. Phys. Chem. Soc.*, 1926, **58**, 1018; **A.**, 437.

<sup>73</sup> L. A. Sarver, *J. Amer. Chem. Soc.*, 1927, **49**, 1472; **B.**, 557.

<sup>74</sup> F. Zetzsche and M. Nachmann, *Helv. Chim. Acta*, 1926, **9**, 979; **A.**, 1927, 127. Compare *idem, ibid.*, p. 420; **A.**, 1926, 705.

<sup>75</sup> A. Pinkus and E. Belche, *Bull. Soc. chim. Belg.*, 1927, **36**, 277; **A.**, 639.

and also for the colorimetric determination of traces of aluminium by observation of the colloidal solutions which this reagent gives with small quantities; the solution appears yellow by transmitted and blue by reflected light.<sup>76</sup> Aluminium is precipitated by 8-hydroxyquinoline from dilute acetic acid and from ammoniacal tartrate solution, but not from solutions containing alkali hydroxides; the crystalline precipitate,  $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$ , can be dried at  $110^\circ$  for weighing, or may be dissolved in hydrochloric acid and the hydroxyquinoline determined bromometrically.<sup>77</sup>

Cobalt can be rapidly determined by suitable treatment of the precipitate given by pyridine and thiocyanate, whereby the compound is weighed as such;<sup>78</sup> a similar process is described in the case of nickel.<sup>79</sup> The magenta colour given by acid or neutral nickel solutions with potassium dithio-oxalate is utilised for the colorimetric determination of nickel; iron and cobalt must be removed.<sup>80</sup> Diphenylamine, or better diphenylbenzidine, may be used as an internal indicator for the titration of zinc salts by ferrocyanide; a small amount of ferricyanide must be present.<sup>81</sup> Zinc is a member of the "oxine" group of metals (*vide supra*), being precipitated by 8-hydroxyquinoline from caustic alkaline tartrate solution as well as from ammoniacal and acetic acid solution.<sup>82</sup> In the separation of manganese from iron by precipitation as pyrophosphate, the presence of considerable quantities of acetate, sulphate, potassium, or sodium ions causes high results.<sup>83</sup> Quantitative oxidation of bivalent manganese to permanganate is effected by nickel peroxide; the process is carried out in two stages, but in the presence of ferric, chromium, and lead salts and more than 5 mg. of cobalt, some modification is necessary.<sup>84</sup>

Neutral barium solutions may be titrated with standard chromate solution, with silver nitrate as internal indicator;<sup>85</sup> a method has been worked out for the micro-titration of barium with chromate (or *vice versa*) depending upon the appearance (or disappearance) of the yellow colour due to the chromate ion.<sup>86</sup> A scheme for the

<sup>76</sup> M. L. de Brouckère and E. Belche, *Bull. Soc. chim. Belg.*, 1927, **36**, 288; **A.**, 640.

<sup>77</sup> F. L. Hahn and K. Vieweg, *Z. anal. Chem.*, 1927, **71**, 122; **A.**, 639; R. Berg, *ibid.*, p. 361; **A.**, 848.

<sup>78</sup> G. Spacu and J. Dick, *ibid.*, p. 97; **A.**, 640.

<sup>79</sup> *Idem*, *ibid.*, p. 442; **A.**, 1047.

<sup>80</sup> L. T. Fairhall, *J. Ind. Hygiene*, 1926, **8**, 528; **A.**, 1927, 127.

<sup>81</sup> W. H. Cone and L. C. Cady, *J. Amer. Chem. Soc.*, 1927, **49**, 356; **A.**, 331; I. M. Kolthoff, *Chem. Weekblad*, 1927, **24**, 203; **A.**, 535.

<sup>82</sup> Hahn and Vieweg, *loc. cit.*; R. Berg, *Z. anal. Chem.*, 1927, **71**, 171; **A.**, 745.

<sup>83</sup> D. Balarev and N. Desev, *ibid.*, 1927, **70**, 444; **A.**, 537.

<sup>84</sup> R. Lang, *Z. anorg. Chem.*, 1928, **158**, 370; **A.**, 1927, 126.

<sup>85</sup> R. F. Le Guyon, *Bull. Soc. chim.*, 1927, [iv], **41**, 99; **A.**, 223.

<sup>86</sup> *Idem*, *Compt. rend.*, 1927, **184**, 945; **A.**, 537.

quantitative separation of calcium, strontium, and barium has been described; <sup>87</sup> potassium oxalate is preferred to the ammonium salt for the precipitation of calcium or strontium. The conditions most favourable for the precipitation of pure calcium oxalate prior to the volumetric determination by permanganate have been worked out. <sup>88</sup> The ignition of calcium oxalate to oxide is greatly hastened by heating in a current of oxygen; <sup>89</sup> this also applies to the conversion of magnesium ammonium phosphate to the pyrophosphate. Calcium can be directly determined in the presence of strontium and barium by titration with standard ferrocyanide in a solution containing half its volume of alcohol, ammonium molybdate being used as external indicator. <sup>90</sup>

Magnesium is another member of the "oxine" group of metals (*vide supra*), being precipitated from alkaline-tartrate solutions by 8-hydroxyquinoline; it is not precipitated from acetic acid solutions and is thus readily separated from the other metals of this group. <sup>91</sup> Two studies have been made of the determination of magnesium by the usual methods. <sup>92</sup>

The reactions involved in the conversion of alkali chlorides into carbonates by means of oxalic acid are not quantitative. <sup>93</sup> A method is described for the determination of sodium as the triple acetate with magnesium and uranium. <sup>94</sup>

Improvements in the iodometric determination of vanadium are described; <sup>95</sup> volumetric methods are recorded based on the reduction of vanadic acid to the vanadous state by liquid amalgams of zinc or lead, followed by appropriate titrations. <sup>96</sup> Sexavalent tungsten is similarly determined after reduction to the quadrivalent state with lead amalgam. Vanadium may be separated from tungsten by precipitation with "cupferron" in the presence of fluoride; <sup>97</sup> but if the amount of vanadium is small, a large amount of ammonium chloride should be present to assist the separation. <sup>98</sup>

<sup>87</sup> L. Szebellédy, *Z. anal. Chem.*, 1927, **70**, 39; **A.**, 223.

<sup>88</sup> F. L. Hahn and G. Weiler, *ibid.*, p. 1; **A.**, 222.

<sup>89</sup> R. Cernatesco and (Mlle.) E. Văscăutan, *Ann. sci. Univ. Jassy*, 1927, **14**, 305; **A.**, 535.

<sup>90</sup> T. Gaspar y Arnal, Diss., Madrid, 1923; **A.**, 1927, 846.

<sup>91</sup> Hahn and Vieweg, *loc. cit.*; R. Berg, *Z. anal. Chem.*, 1927, **71**, 23; **A.**, 639.

<sup>92</sup> A. Tereschenko and M. Necritche, *Ukraine Chem. J.*, 1926, **2**, 163; **A.**, 1927, 535; F. L. Hahn, K. Vieweg, and H. Meyer, *Ber.*, 1927, **60**, [B], 971; **A.**, 535.

<sup>93</sup> L. N. Muravlev, *Z. anal. Chem.*, 1927, **72**, 15; **A.**, 1046; *Z. anorg. Chem.*, 1927, **165**, 137; **A.**, 953.

<sup>94</sup> D. I. Perieteanu, *Bul. Soc. chim. România*, 1927, **9**, 17; **A.**, 1046.

<sup>95</sup> J. B. Ramsey, *J. Amer. Chem. Soc.*, 1927, **49**, 1138; **A.**, 640.

<sup>96</sup> K. Someya, *Z. anorg. Chem.*, 1927, **163**, 206; **A.**, 746; *Sci. Rep. Tōhoku Imp. Univ.*, 1927, **16**, 521; **A.**, 848.

<sup>97</sup> S. G. Clarke, *Analyst*, 1927, **52**, 466; **B.**, 752.

<sup>98</sup> *Idem*, *ibid.*, p. 527; **A.**, 1048.

Some observations have been made on methods, both volumetric and gravimetric, for the determination of cerium.<sup>99</sup> Aluminium is quantitatively separated from beryllium by treating a hot solution of the metals as sulphates with saturated ammonium acetate solution containing 30% of pure tannin.<sup>1</sup> The conditions for the precipitation of titanium with "cupferron" in the presence of uranium have been examined,<sup>2</sup> and also for the determination of thallium as chromate, methods of separation from other metals being described.<sup>3</sup> Hafnium and zirconium have been separated by repeated precipitation of the phosphates from sulphuric acid solution,<sup>4</sup> and also by fractional decomposition of the complex phosphatofluoro-hafnates and -zirconates.<sup>5</sup>

A study of the precipitation of tungsten by tannin has been made,<sup>6</sup> and also of the separation of tungsten from tantalum and niobium, advantage being taken of the solubility of sodium tungstate in solutions of high sodium-ion concentration in which the tantalate and niobate are practically insoluble.<sup>7</sup>

Improvements have been made in a method of analysis of mixtures of sulphide, sulphite, and thiosulphate,<sup>8</sup> and also of mixtures of tri-, tetra-, and penta-thionates.<sup>9</sup> Methods involving elimination of sulphides, sulphites, etc., by boiling with hydrochloric acid in an inert atmosphere tend to give high results for sulphate. It is therefore recommended that sulphides be removed by freshly precipitated zinc carbonate in the presence of glycerol, sulphites fixed by addition of formaldehyde and acetic acid, and thiosulphates by iodine, barium sulphate being then precipitated from cold acetic acid solution.<sup>10</sup> Other investigations have also been made of the determination of the sulphate ion as barium sulphate,<sup>11</sup> and the alkalimetric titration of precipitated benzidine sulphate has likewise been examined.<sup>12</sup> *pp'*-Diaminodiphenylamine is used as an indicator for the back-titration with dichromate of the excess of

<sup>99</sup> R. Lessnig, *Z. anal. Chem.*, 1927, **71**, 161; *A.*, 746; T. Lindeman and M. Hafstad, *ibid.*, **70**, 433; *A.*, 536.

<sup>1</sup> L. Moser and M. Niesse, *Monatsh.*, 1927, **48**, 113; *A.*, 846.

<sup>2</sup> A. Angeletti, *Ann. Chim. Appl.*, 1927, **17**, 53; *A.*, 333.

<sup>3</sup> L. Moser and A. Brukl, *Monatsh.*, 1926, **47**, 709; *A.*, 1927, 436.

<sup>4</sup> J. H. de Boer, *Z. anorg. Chem.*, 1927, **165**, 16; *A.*, 954.

<sup>5</sup> J. H. de Boer and P. Koets, *ibid.*, p. 21; *A.*, 954.

<sup>6</sup> W. R. Schoeller and C. Jahn, *Analyst*, 1927, **52**, 504; *A.*, 1047.

<sup>7</sup> *Idem*, *ibid.*, p. 506; *A.*, 1047; *ibid.*, 1926, **51**, 613; *A.*, 1927, 32.

<sup>8</sup> A. Kurtenacker and R. Wollak, *Z. anorg. Chem.*, 1927, **161**, 201; *A.*, 534.

<sup>9</sup> A. Kurtenacker and E. Goldbach, *ibid.*, 1927, **166**, 177; *A.*, 1045.

<sup>10</sup> A. Kurtenacker and R. Wollak, *Z. anal. Chem.*, 1927, **71**, 37; *A.*, 638.

<sup>11</sup> V. Marjanović, *Arhiv Hemiju*, 1927, **1**, 5; *A.*, 744; F. G. Germuth, *Amer. J. Pharm.*, 1927, **99**, 271; *A.*, 638.

<sup>12</sup> L. W. Haase, *Z. angew. Chem.*, 1927, **40**, 595; *A.*, 638; M. Talenti, *Giorn. Chim. Ind. Appl.*, 1926, **8**, 611; *A.*, 1927, 330.

barium chloride used in volumetric determination of sulphates.<sup>13</sup> For the determination of concentrated sulphurous acid solutions, a more powerful oxidising agent than iodine is recommended; hypochlorite is used, excess being titrated iodometrically.<sup>14</sup> This reagent is similarly applied to the determination of cyanides and of thiocyanate.<sup>15</sup> A volumetric determination of selenium and tellurium in the same solution depends on the oxidation of the dioxides to trioxides by permanganate and of tellurium dioxide alone to trioxide by dichromate.<sup>16</sup>

Errors in the ordinary gasometric method of determining nitrates and nitrites are compensated by carrying out a blank determination under identical conditions, using a quantity of pure potassium nitrate containing about the same quantity of nitrogen as the sample, and making due allowance for the deficiency found.<sup>17</sup> Attention is called to the fact that certain compounds, in particular caffeine and theobromine, when digested with sulphuric acid containing potassium and copper sulphates, yield appreciable quantities of methylamine.<sup>18</sup> An iodometric method for the determination of azoimide has been described.<sup>19</sup>

Although the precipitate obtained when phosphine reacts with mercuric chloride is of variable character, the quantity of hydrogen chloride formed bears a definite ratio to the volume of phosphine and therefore affords a method of determination.<sup>20</sup> The reaction of elementary phosphorus with potassium iodate in acid solution, whereby iodine is liberated, forms the basis of a method for determining the element.<sup>21</sup> 1 : 2 : 5 : 8-Tetrahydroxyanthraquinone may be used as indicator in the titration of an ammoniacal solution of phosphate with standard magnesium solution,<sup>22</sup> whilst magnesium is determined by precipitation with a standard phosphate solution, the excess of which is then determined as above. A study of the determination of phosphate by precipitation as magnesium ammonium phosphate has been made,<sup>23</sup> and also of the precipitation of phosphate with reference to hydrogen-ion concentration.<sup>24</sup>

<sup>13</sup> H. Roth, *Z. angew. Chem.*, 1926, **39**, 1599; **A.**, 1927, 125.

<sup>14</sup> J. Bicskei, *Z. anorg. Chem.*, 1927, **160**, 64; **A.**, 330.

<sup>15</sup> *Idem, ibid.*, p. 271; **A.**, 331.

<sup>16</sup> Z. Littman, *Chem. Ztg.*, 1927, **51**, 323; **A.**, 534.

<sup>17</sup> A. Pinkus and J. Jacobi, *Bull. Soc. chim. Belg.*, 1927, **36**, 448; **A.**, 952.

<sup>18</sup> B. Sjollesma and L. Seekles, *Biochem. Z.*, 1927, **183**, 240; **A.**, 583.

<sup>19</sup> J. Martin, *J. Amer. Chem. Soc.*, 1927, **49**, 2133; **A.**, 1046.

<sup>20</sup> M. Wilmet, *Compt. rend.*, 1927, **185**, 206; **A.**, 846.

<sup>21</sup> T. F. Buehrer and O. E. Schupp, jun., *J. Amer. Chem. Soc.*, 1927, **49**, 9; **A.**, 222.

<sup>22</sup> F. L. Hahn and H. Meyer, *Ber.*, 1927, **60**, [B], 975; **A.**, 534.

<sup>23</sup> W. M. McNabb, *J. Amer. Chem. Soc.*, 1927, **49**, 891; **A.**, 435.

<sup>24</sup> H. T. S. Britton, *J.*, 1927, 614.



In the iodometric titration of arsenate, considerable advantage accrues by working in concentrated hydrochloric acid solutions; <sup>25</sup> ignition of magnesium ammonium arsenate to the pyroarsenate should be carried out at 500—600°. <sup>26</sup> Arsenites are accurately and rapidly determined by distillation with methyl alcohol saturated with hydrogen chloride, the removal of the arsenic trichloride being favoured by the presence of powdered quartz or of potassium bromide. <sup>27</sup>

Bromide and iodide ions may be removed, prior to the determination of chloride, by treating the acidified solution with bromic acid in presence of acetone. The bromine and iodine liberated form, with the acetone, derivatives from which the halogen is not precipitated by silver nitrate. <sup>28</sup> A similar method is applied to the determination of iodide in presence of chloride and bromide (provided that the quantity of the latter is not large), titration of the acidified solution containing acetone being carried out with standard iodate solution. <sup>29</sup> A combination of the two processes permits of the determination of the three halides in admixture, the bromide being found by difference.

A most interesting development in the determination of halides is the application <sup>30</sup> of certain dyestuffs as indicators. These act by adsorption on the colloidal particles of the silver halide. As soon as excess of silver ion is present, a salt of the dye with silver is formed, which is different in colour from the adsorbed dyestuff, but which must be more soluble than the silver halide itself in order that a sharp colour change may be given. <sup>31</sup> It has not been possible to ascertain directly the extent of the indicator effect, but it is not as great as that in Mohr's titration using chromate. <sup>32</sup> Fajans used fluorescein for the titration of chlorides and dibromofluorescein or eosin for bromides and iodides; the method gives excellent results in neutral or acetic acid solutions, provided that no great quantity of a strong electrolyte is present. <sup>33</sup> The determination of iodide in

<sup>25</sup> K. Böttger and W. Böttger, *Z. anal. Chem.*, 1927, **70**, 97; *A.*, 222.

<sup>26</sup> W. M. McNabb, *J. Amer. Chem. Soc.*, 1927, **49**, 1451; *A.*, 745.

<sup>27</sup> L. A. Deshusses and J. Deshusses, *Helv. Chim. Acta*, 1927, **10**, 517; *A.*, 744.

<sup>28</sup> R. Berg, *Z. anal. Chem.*, 1926, **69**, 342; *A.*, 1927, 35.

<sup>29</sup> *Idem*, *ibid.*, p. 369; *A.*, 1927, 124.

<sup>30</sup> K. Fajans and O. Hassel, *Z. Elektrochem.*, 1923, **29**, 495; *A.*, 1924, ii, 60; K. Fajans and H. Wolff, *Z. anorg. Chem.*, 1924, **137**, 221; *A.*, 1924, ii, 776.

<sup>31</sup> R. H. Burschtein, *Z. anorg. Chem.*, 1927, **164**, 219; *A.*, 847; *J. Russ. Phys. Chem. Soc.*, 1927, **59**, 521; *A.*, 1159.

<sup>32</sup> W. Böttger and K. O. Schmitt, *Z. anorg. Chem.*, 1924, **137**, 246; *A.*, 1924, ii, 776.

<sup>33</sup> I. M. Kolthoff and L. H. van Berk, *Z. anal. Chem.*, 1927, **70**, 369; *A.*, 434.

the presence of chloride can be effected by the use of eosin as indicator, preferably in the presence of ammonium carbonate;<sup>34</sup> bromides interfere with the titration. Among other dyes investigated in connexion with this method are methyl-violet,<sup>35</sup> metanil-yellow and bromophenol-blue.<sup>36</sup>

The process has been applied to the determination of other radicals than the halides; thus fluorescein or eosin may be used for the titration of thiocyanate with silver,<sup>33</sup> and sodium alizarin-sulphonate for ferrocyanide with lead.<sup>31</sup>

### *Organic Analysis.*

*Qualitative.*—Iodine, generated by reaction of hypochlorite with potassium iodide gives with amines a yellow coloration but no precipitate, and with amides a yellow, red, or grey precipitate;<sup>37</sup> with ammonium salts a black precipitate of nitrogen iodide is formed. Several toluene- $\omega$ -sulphonamides are described, suitable for the identification of amines.<sup>38</sup> The colours developed when nitrous gases react with mercaptans in solution in organic solvents serve as a test for the thiol-group.<sup>39</sup>

For the detection of methyl alcohol after oxidation to formaldehyde, potassium guaiacolsulphonate is preferable to guaiacol, as the former does not react with acetaldehyde but gives the formaldehyde reaction equally readily.<sup>40</sup> A survey of the various methods for the detection of methyl alcohol in the presence of ethyl alcohol has been made.<sup>41</sup>

The formation of a white precipitate (of pentabromoacetone) with bromine after a preliminary oxidation with permanganate serves to detect citric acid in the presence of other organic acids or of chlorides, unless these are in great excess;<sup>42</sup> a microchemical test for citric acid in the presence of tartaric, malic, succinic, lactic, and oxalic acids depends on the formation of iodoacetone.<sup>43</sup>

Summaries have been made of the reactions and optical properties

<sup>34</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1927, **70**, 395; *A.*, 435.

<sup>35</sup> J. Hodakow, *Z. physikal. Chem.*, 1927, **127**, 43; *A.*, 743.

<sup>36</sup> I. M. Kolthoff, *Z. anal. Chem.*, 1927, **71**, 235; *A.*, 744.

<sup>37</sup> J. A. Sanchez, *Anal. Asoc. Quím. Argentina*, 1926, **14**, 366; *A.*, 1927, 552.

<sup>38</sup> C. S. Marvel and H. B. Gillespie, *J. Amer. Chem. Soc.*, 1926, **48**, 2943; *A.*, 1927, 66.

<sup>39</sup> H. Rheinboldt, *Ber.*, 1927, **60**, [B], 184; *A.*, 227; H. Lecher and W. Siefken, *ibid.*, 1926, **59**, [B], 2594; *A.*, 1927, 39.

<sup>40</sup> H. Matthes, *Pharm. Ztg.*, 1926, **71**, 1508; *A.*, 1927, 66; R. Bauer, *ibid.*, p. 1543; *A.*, 1927, 66.

<sup>41</sup> L. O. Wright, *Ind. Eng. Chem.*, 1927, **19**, 750; *A.*, 687.

<sup>42</sup> N. Schoorl, *Pharm. Weekblad*, 1926, **63**, 1455; *A.*, 1927, 166.

<sup>43</sup> M. Wagenaar, *Chem. Weekblad*, 1927, **24**, 258; *A.*, 647.

of codeine,<sup>44</sup> and of the delicacy of the reactions for caffeine, theobromine, strychnine, brucine, quinine, and morphine.<sup>45</sup> An alkaline solution of uric acid or other purine derivative gives with *p*-aminophenol or metol in the presence of an oxidising agent such as sodium persulphate, a yellow coloration which is not affected by the presence of dextrose or of proteins.<sup>46</sup>

The furfuraldehyde reaction is given by both ketonic and aldehydic methylpentoses.<sup>47</sup> Chlorophyll in ethereal solution, when illuminated by ultra-violet radiation from a quartz lamp, exhibits a vivid red fluorescence, not given by carotin or by xanthophyll.<sup>48</sup>

Piperidine reacts more readily and clearly than other reagents with the labile halogen atoms of aryl halogenonitro-compounds.<sup>49</sup> The development of the colour produced by the action of nitrous acid on phenol, best at  $p_H$  4—5, is greatly accelerated by the presence of mercury salts,<sup>50</sup> whilst the blue colour due to indophenol formation by the action of 2 : 6-dibromobenzoquinonechloroimide on phenol, preferably at  $p_H$  9—10, serves to detect the latter in a concentration of 1 in 20,000,000.<sup>51</sup> The colour reactions obtained by the interaction of a number of common phenols and aldehydes in the presence of alcohol and sulphuric acid are tabulated.<sup>52</sup>

The reddish coloration which develops when an equimolecular mixture of benzene- or other sulphonyl chloride with pyridine or its homologues is treated with caustic potash solutions constitutes an exceedingly delicate reaction for these bases. The colours, which are not given by other cyclic bases, are discharged by light and by oxidising agents in the cold.<sup>53</sup>

The methyl and ethyl ethers of thymol in acid solution react with sodium nitrite to give nitrosothymol, whereas the ethyl ethers of carvacrol, *o*-cresol, and anisole yield no nitroso-derivatives.<sup>54</sup> Optical data for the benzyl- $\psi$ -thiocarbamide salts of naphthalene-mono- and certain -di-sulphonic acids are given as an aid to the identification of the acids by microscopical examination.<sup>55</sup>

<sup>44</sup> M. Wagenaar, *Pharm. Weekblad*, 1927, **64**, 671; **A.**, 785.

<sup>45</sup> A. Heiduschka and N. I. Meisner, *Arch. Pharm.*, 1927, **265**, 455; **A.**, 785.

<sup>46</sup> E. Pittarelli, *Arch. Farm. speriment. Sci. aff.*, 1927, **43**, 142; **A.**, 979.

<sup>47</sup> E. Votoček and F. Rác, *Chem. Listy*, 1927, **6**, 231; **A.**, 688.

<sup>48</sup> P. W. Danckworth and E. Pfau, *Arch. Pharm.*, 1927, **265**, 560; **A.**, 1101.

<sup>49</sup> R. J. W. Le Fèvre and E. E. Turner, *J.*, 1927, 113.

<sup>50</sup> H. D. Gibbs, *J. Biol. Chem.*, 1927, **71**, 445; **A.**, 475.

<sup>51</sup> *Idem*, *ibid.*, 1927, **72**, 649; **A.**, 688.

<sup>52</sup> L. Ekkert, *Pharm. Zentr.*, 1927, **68**, 563; **A.**, 984.

<sup>53</sup> E. Gebauer-Fülneegg and F. Riesenfeld, *Monatsh.*, 1926, **47**, 185; **A.**, 1927, 139.

<sup>54</sup> F. W. Klingstedt and E. Sundstrom, *J. pr. Chem.*, 1927, [ii], **116**, 307; **A.**, 1065.

<sup>55</sup> R. M. Hann and G. L. Keenan, *J. Physical Chem.*, 1927, **31**, 1082; **A.**, 866

*Quantitative.*—An investigation into the possible sources of error in organic elementary analysis has shown that, although the absorption of carbon dioxide by lead dioxide may generally be ignored, error may be produced thereby in some circumstances;<sup>56</sup> the several sources from which small amounts of carbon dioxide may be introduced are indicated.<sup>57</sup> Rubber is capable of absorbing very volatile foreign organic substances; cork absorbs moisture and carbon dioxide; and lubricants should be applied judiciously.<sup>58</sup> Various devices are adopted to decrease the time necessary to determine the carbon in a number of organic substances by boiling with acid permanganate, the resultant carbon dioxide being measured;<sup>59</sup> the same principle is applied for micro-quantitative work, oxidation being effected by a sulphuric acid solution of potassium dichromate and silver chromate containing sodium sulphate.<sup>60</sup> The combustion of a number of organic compounds by chromic acid mixture has been investigated.<sup>61</sup> Certain modifications of Pregl's micro-combustion method have also been made.<sup>62</sup>

Nitrogen may be determined in organic substances, other than azo- and diazo-compounds, by Devarda's method after wet combustion with acid permanganate in the presence of platinum; for the determination of halogens, the oxidation is carried out in the presence of silver nitrate.<sup>63</sup> A modification of the direct combustion method has been made for the determination of bromine in both aromatic and aliphatic compounds.<sup>64</sup> An arrangement to obviate the tendency of solid compounds to distil unchanged through the reduction tube in ter Meulen's catalytic hydrogenation process for the determination of nitrogen is described.<sup>65</sup>

Selenium in organic compounds is determined after oxidation in a Parr bomb by sodium peroxide in the presence of a little sucrose and potassium nitrate;<sup>66</sup> cacodylic acid or triphenylphosphine are decomposed by heating with sulphuric acid and potassium persulphate prior to the determination of arsenic or phosphorus respectively.<sup>67</sup>

<sup>56</sup> J. Lindner, *Ber.*, 1926, **59**, [B], 2561; *A.*, 1927, 66.

<sup>57</sup> *Idem*, *ibid.*, p. 2806; *A.*, 1927, 166.

<sup>58</sup> *Idem*, *ibid.*, 1927, **60**, [B], 124; *A.*, 269.

<sup>59</sup> B. Lustig, *Biochem. Z.*, 1927, **184**, 67; *A.*, 687.

<sup>60</sup> M. Nicloux, *Compt. rend.*, 1927, **184**, 890; *A.*, 436.

<sup>61</sup> T. von Fellenberg, *Biochem. Z.*, 1927, **188**, 365; *A.*, 1100.

<sup>62</sup> G. Kemmerer and L. T. Hallett, *Ind. Eng. Chem.*, 1927, **19**, 173; *A.*, 269.

<sup>63</sup> B. Lustig, *Biochem. Z.*, 1927, **185**, 349; *A.*, 891.

<sup>64</sup> F. L. Smith, *Philippine J. Sci.*, 1927, **32**, 315; *A.*, 551.

<sup>65</sup> F. L. Smith and A. P. West, *ibid.*, 1926, **31**, 265; *A.*, 1927, 166.

<sup>66</sup> E. H. Shaw and E. E. Reid, *J. Amer. Chem. Soc.*, 1927, **49**, 2330; *A.*, 1101.

<sup>67</sup> R. Poggi and A. Polverini, *Atti R. Accad. Lincei*, 1926, [vi], **4**, 315; *A.*, 1927, 66.

Acetylation with acetic anhydride and pyridine is applied to the volumetric determination of hydroxyl groups in sugars and other organic compounds.<sup>68</sup> A modification of the ordinary Zeisel process has been made to permit of the determination of the methoxyl groups being made in the presence of aldehydes.<sup>69</sup> It is proposed to substitute thiosulphate solution containing cadmium sulphate for red phosphorus in the micro-determination of methoxyl, and also to make a small correction to allow for the low results due to incomplete reaction between the alkyl iodide and silver nitrate.<sup>70</sup> The carbonyl group in aldehydes and ketones is determined by treatment with phenylhydrazine, the excess being ascertained by measuring the nitrogen evolved after oxidation with Fehling's solution.<sup>71</sup> Secondary nitrosoamines may be determined by measuring the nitric oxide evolved on boiling with ferrous chloride and hydrochloric acid; reduction by mercury and concentrated sulphuric acid is seldom quantitative, often by reason of partial conversion into *C*-nitroso-compounds.<sup>72</sup>

Methyl chloride is determined by conversion into the iodide by treatment under pressure in absolute-alcoholic solution with *sodium* iodide; the iodide is then distilled, and precipitated as the compound  $\text{CH}_3\text{I}, \text{AgNO}_3$ ; the silver iodide obtained by hydrolysis amounts to 94% of the theoretical.<sup>73</sup> Small quantities of ethyl iodide in air or in very dilute solution are determined by keeping in contact with standard silver nitrate solution in concentrated nitric acid.<sup>74</sup> The pink colour obtained by heating solutions containing chloroform with pyridine in the presence of sodium hydroxide has been applied to the colorimetric evaluation of very dilute aqueous solutions of chloroform.<sup>75</sup>

*iso*Propyl alcohol may be readily determined in the presence of acetone by quantitative oxidation to acetone by chromic acid, followed by back-titration of the excess.<sup>76</sup> Modifications of the usual method for determining diacetyl and acetylmethylcarbinol as nickel dimethylglyoxime are described.<sup>77</sup> Formic acid may be determined bromometrically either directly or after reduction of mercuric to mercurous chloride.<sup>78</sup> A mercury method for the

<sup>68</sup> V. L. Peterson and E. S. West, *J. Biol. Chem.*, 1927, **74**, 379; **A.**, 1100.

<sup>69</sup> K. Wiesler, *Z. angew. Chem.*, 1927, **40**, 975; **A.**, 1101.

<sup>70</sup> A. Friedrich, *Z. physiol. Chem.*, 1927, **163**, 141; **A.**, 475.

<sup>71</sup> G. W. Ellis, *J.*, 1927, 848.

<sup>72</sup> K. Lehmstedt, *Ber.*, 1927, **60**, [B], 1910; **A.**, 1062.

<sup>73</sup> K. Roka and O. Fuchs, *Z. anal. Chem.*, 1927, **71**, 381; **A.**, 984.

<sup>74</sup> I. Starr, jun., and C. J. Gamble, *J. Biol. Chem.*, 1927, **71**, 509; **A.**, 270.

<sup>75</sup> W. H. Cole, *J. Biol. Chem.*, 1926, **71**, 173; **A.**, 1927, 270.

<sup>76</sup> H. A. Cassar, *Ind. Eng. Chem.*, 1927, **19**, 1061; **A.**, 1100.

<sup>77</sup> C. B. van Niel, *Biochem. Z.*, 1927, **187**, 472; **A.**, 1101.

<sup>78</sup> F. Oberhauser and W. Hensinger, *Z. anorg. Chem.*, 1927, **160**, 366; **A.**, 475.

determination of acetone has been described,<sup>79</sup> whilst dihydroxy-acetone may be determined in solution by comparison of the time required for incipient reduction of Fehling's solution under standard conditions with that required for solutions of known concentration.<sup>80</sup> Hexamethylenetetramine is evaluated by precipitation with picric acid and determining the excess of reagent.<sup>81</sup>

Xylose and the *d*-ribose of purine nucleotides are quantitatively converted into furfuraldehyde by distillation with 20% hydrochloric acid for 3 hours; under these conditions the pyrimidine nucleotides yield only small amounts of furfural.<sup>82</sup> Dextrose is readily oxidised by iodine to gluconic acid at ordinary temperatures in a strongly alkaline medium.<sup>83</sup>

Allantoic acid is converted by acid hydrolysis to carbamide which is then precipitated as xanthylcarbamide.<sup>84</sup>  $\psi$ -Morphine is completely precipitated by silicotungstic acid from solutions at  $p_H$  7.8, morphine being precipitated on acidifying the filtrate.<sup>85</sup>

The use of freshly precipitated silver oxide in the presence of sulphuric acid for the precipitation of bases is preferred to that of silver nitrate or sulphate.<sup>86</sup> By adjustment of a solution containing histidine and arginine, together with excess of a soluble silver salt, to  $p_H$  7.0, the silver compound of histidine is completely precipitated; treatment of the filtrate with barium hydroxide to  $p_H$  10–11 results in the precipitation of the silver compound of arginine.<sup>87</sup> Arginine is completely converted into carbamide by arginase in a medium of  $p_H$  9.9.<sup>88</sup> Titration of an amino-acid in 80% alcoholic solution with sodium hydroxide to a blue colour with thymolphthalein gives an accurate measure of the carboxyl groups; back-titration of the resulting solution with hydrochloric acid to a red colour with methyl-red determines the amount of amino-compounds.<sup>89</sup>

Pure cystine is precipitated to the extent of 97% by phosphotungstic acid.<sup>90</sup>

Addition of lithium sulphate, as well as sodium carbonate and cyanide, prevents the formation of turbidity during the colorimetric

<sup>79</sup> A. Ionesco-Matiu, *Ann. sci. Univ. Jassy*, 1927, **14**, 363; **A.**, 687.

<sup>80</sup> H. Schmalfuss, *Ber.*, 1927, **60**, [B], 1045; **A.**, 687.

<sup>81</sup> (Mrs.) C. Kollo and B. N. Angelescu, *Bul. Soc. chim. România*, 1926, **8**, 17; **A.**, 1927, 786.

<sup>82</sup> W. S. Hoffman, *J. Biol. Chem.*, 1927, **73**, 15; **A.**, 687.

<sup>83</sup> A. Voorhies and A. M. Alvarado, *Ind. Eng. Chem.*, 1927, **19**, 848; **A.**, 891.

<sup>84</sup> R. Fosse and (Mlle.) V. Bossuyt, *Compt. rend.*, 1927, **185**, 308; **A.**, 891.

<sup>85</sup> A. K. Balls, *J. Biol. Chem.*, 1927, **71**, 537, 543; **A.**, 264.

<sup>86</sup> A. Kresel, *Z. physiol. Chem.*, 1926, **161**, 147; **A.**, 1927, 270.

<sup>87</sup> H. B. Vickery and C. S. Leavenworth, *J. Biol. Chem.*, 1927, **72**, 403; **A.**, 546.

<sup>88</sup> A. Bonot and T. Cahn, *Compt. rend.*, 1927, **184**, 246; **A.**, 269.

<sup>89</sup> R. Martens, *Bull. Soc. Chim. biol.*, 1927, **9**, 454; **A.**, 687.

<sup>90</sup> R. H. A. Plimmer and J. Lowndes, *Biochem. J.*, 1927, **21**, 247; **A.**, 269.

determination of tyrosine with Folin and Looney's phenol reagent; the depth of colour given by tyrosine and tryptophan is in inverse proportion to their molecular weights.<sup>91</sup> Tyrosine itself, however, is more conveniently determined by a modification of Millon's reaction.<sup>91, 92</sup> The conversion of *l*- $\alpha$ -amino- $\beta$ -3 : 4-dihydroxy-phenylpropionic acid into melanin without flocculation in very dilute solution serves for the colorimetric determination of the amino-acid; the method can be applied in the presence of tyrosine.<sup>93</sup> Diketopiperazines may be determined with fair accuracy in the presence of amino-acids and peptides by Siegfried's carbamate reaction.<sup>94</sup>

The amino-nitrogen in nitroaniline and nitroacetanilide is obtained as ammonia by refluxing with sodium hydroxide solution.<sup>95</sup> Phenyl-acetylene is determined by weighing the copper compound precipitated from alcoholic solution by ammoniacal cuprous chloride solution.<sup>96</sup>

#### *Physical Methods.*

The variation in size of the absorption bands of neutral and of nitric acid solutions of neodymium and of praseodymium alone and in admixture has been applied to the quantitative analysis of mixtures of these two elements.<sup>97</sup> The characteristic absorption bands of the nitrite and nitrate ions in the ultra-violet region serve for the detection of these ions in admixture with other common anions; for the detection of the weaker nitrate band in the presence of nitrites, the latter are first decomposed by carbamide. Determination of the extinction coefficients for specified regions serves for the quantitative measurement of these anions.<sup>98</sup> Extinction coefficients have been determined for the copper salt of coproporphyrin in sodium hydroxide and for hæmin, hæmochromogen, and coproporphyrin in solution in pyridine. The pyridine must be specially purified for quantitative work, though it need not be anhydrous.<sup>99</sup> Tables are given for the spectrophotometric determination of glycuronic acid and its menthol derivative.<sup>1</sup>

<sup>91</sup> O. Folin and V. Ciocalteu, *J. Biol. Chem.*, 1927, **73**, 627; **A.**, 892.

<sup>92</sup> D. Zuverkalov, *Z. physiol. Chem.*, 1927, **163**, 185; **A.**, 688.

<sup>93</sup> H. Schmalfuss and H. Lindemann, *Biochem. Z.*, 1927, **184**, 10; **A.**, 688.

<sup>94</sup> A. Blanchetière, *Bull. Soc. chim.*, 1927, [iv], **41**, 101; **A.**, 269; Siegfried, *Z. physiol. Chem.*, 1905, **44**, 85; *A.*, 1905, ii, 33; *Ber.*, 1906, **39**, 401; *A.*, 1906, i, 144.

<sup>95</sup> N. Semiganovsky, *Z. anal. Chem.*, 1927, **72**, 27; **A.**, 1062.

<sup>96</sup> F. Hein and A. Meyer, *ibid.*, p. 30; **A.**, 1100.

<sup>97</sup> E. Delauney, *Compt. rend.*, 1927, **185**, 354; **A.**, 847.

<sup>98</sup> J. Eisenbrand, *Pharm. Ztg.*, 1927, **72**, 672; **A.**, 638.

<sup>99</sup> A. Treibs, *Z. physiol. Chem.*, 1927, **168**, 68; **A.**, 892.

<sup>1</sup> G. Scheff, *Biochem. Z.*, 1927, **183**, 341; **A.**, 551.

The diminution in the intensity of the lines of the arc spectrum of an element as the concentration of that element diminishes is not uniform for the different lines composing the spectrum ;<sup>2</sup> by comparison, however, with mixtures of known concentration, silica being used as the diluent, uranium,<sup>3</sup> vanadium,<sup>4</sup> and tungsten<sup>5</sup> may be determined in ores with fair accuracy. Among other applications of the method may be recorded the determination of lead, bismuth, or cadmium in tin, tin in lead, lead in bismuth,<sup>6</sup> lead in gold and in gold-copper alloys,<sup>7</sup> impurities in aluminium.<sup>8</sup> Attention is directed to the fact that quantitative spectral analysis is beset with pitfalls.<sup>9</sup> A method of determining tantalum by means of the X-ray spectrum has been described.<sup>10</sup> A general review of this subject is available.<sup>11</sup>

### *Electrochemical Methods.*

The water content of glycerol is ascertained by measuring the conductance of potassium chloride.<sup>12</sup> Zinc may be estimated in solutions, not too acid, by determining the conductivity of the solution while adding standard sodium hydroxide.<sup>13</sup> A conductivity method for the determination of carbon dioxide has been described.<sup>14</sup>

*Electrolytic.*—Antimony may be deposited electrolytically in the presence of tin at 60—70° from a solution containing only just sufficient hydrochloric acid to prevent turbidity, a cathode potential of about 0.3 volt being used ; subsequent deposition of tin begins at potential 0.6 volt, the temperature being lowered to 25° and a little hydroxylamine hydrochloride being added.<sup>15</sup> Mercury can be used as cathode in the determination of cobalt, nickel, and the more noble metals.<sup>16</sup> Zinc may be determined accurately by electrolytic means

<sup>2</sup> C. Porlezza and A. Donati, *Ann. Chim. Appl.*, 1926, **16**, 519; **A.**, 1927, 124.

<sup>3</sup> *Idem, ibid.*, p. 622; **A.**, 1927, 184.

<sup>4</sup> *Idem, ibid.*, 1927, **17**, 3; **A.**, 334.

<sup>5</sup> A. Donati, *ibid.*, p. 14; **A.**, 333.

<sup>6</sup> E. Schweitzer, *Z. anorg. Chem.*, 1927, **164**, 127; **165**, 364; **A.**, 845, 1046.

<sup>7</sup> A. Reis, *Ver. Ges. deut. Naturforsch. Aerzte*, 1926, **19**, 1114; **A.**, 1927, 329.

<sup>8</sup> R. Adan, *Bull. Soc. chim. Belg.*, 1926, **35**, 447; **B.**, 1927, 143.

<sup>9</sup> H. Konen, *Ver. Ges. deut. Naturforsch. Aerzte*, 1926, **19**, 1108; **A.**, 1927, 329.

<sup>10</sup> G. von Hevesy and J. Böhm, *Z. anorg. Chem.*, 1927, **164**, 69; **A.**, 849.

<sup>11</sup> P. Günther, *Ver. Ges. deut. Naturforsch. Aerzte*, 1926, **19**, 1118; **A.**, 1927, 329.

<sup>12</sup> N. Kameyama and T. Semba, *J. Soc. Chem. Ind. Japan*, 1927, **30**, 10; **A.**, 330.

<sup>13</sup> G. Sander and O. Pfundt, *Z. angew. Chem.*, 1926, **39**, 1557; **A.**, 1927, 126.

<sup>14</sup> L. E. Bayliss, *Biochem. J.*, 1927, **21**, 662; **A.**, 745.

<sup>15</sup> A. Schleicher and L. Toussaint, *Z. anorg. Chem.*, 1927, **159**, 319; **A.**, 222.

<sup>16</sup> H. S. Lukens, *Trans. Amer. Electrochem. Soc.*, 1927, **51**, 133; **A.**, 533.



in the presence of dilute sulphuric acid if an anode of lead peroxide, supported on platinum, and a cathode of amalgamated brass are used.<sup>17</sup>

*Potentiometric.*—It is suggested that the irregularities observed in the potentiometric curves obtained in the determination of lead, barium, and mercury with chromate, and of cerium, lead, and zinc with ferrocyanide are due to dissolution and ionisation of the precipitate; this may be overcome by the addition of ethyl alcohol.<sup>18</sup> The limits of accuracy of the titration of acids with alkali hydroxides using the quinhydrone electrode have been investigated,<sup>19</sup> and also the effect of gelatin on the titration curves of various acids.<sup>20</sup> Several new forms of electrodes have been described,<sup>21</sup> also an absolute method for titration of strong acids and halides in which no potentiometer, standard cell, or normal electrode is required.<sup>22</sup>

Titrimetric are best carried out when the reagent is added in equal and preferably not excessively small amounts;<sup>23</sup> the graphical method of ascertaining the end-point affords more accurate results than the differential when, as in the case of the titration of iodides with permanganate, the reacting substances are not in equimolecular ratio.<sup>24</sup>

Conditions are described for the titration of antimonious and stannous chlorides successively with chromous chloride;<sup>25</sup> this reducing agent has also been applied to the determination of copper,<sup>26</sup> of mercury,<sup>27</sup> and of molybdenum.<sup>28</sup> Silver and lead together may be determined by titrating first with sodium chloride, using a silver electrode, and then with ferrocyanide, using platinum.<sup>29</sup>

Ferrous solutions can be accurately determined by titration with bromate.<sup>30</sup>

<sup>17</sup> R. Belasio and E. Mellana, *Ann. Chim. Appl.*, 1927, **17**, 336; **A.**, 953.

<sup>18</sup> I. Athanasiu, *Bul. Soc. Romăna Științe*, 1926, **29**, 7; **A.**, 1927, 126.

<sup>19</sup> A. J. Rabinowitsch and V. A. Kargin, *Z. Elektrochem.*, 1927, **33**, 11; **A.**, 221.

<sup>20</sup> E. Little, *J. Amer. Pharm. Assoc.*, 1927, **16**, 414; **A.**, 743.

<sup>21</sup> T. R. Ball, *Ind. Eng. Chem.*, 1927, **19**, 370; **A.**, 434; J. W. Williams and T. A. Whitenack, *J. Physical Chem.*, 1927, **31**, 519; **A.**, 434; I. I. Shukov, *Nature*, 1927, **120**, 14; **A.**, 743; F. Emslander, *Woch. Brau.*, 1927, **44**, 268; **A.**, 743.

<sup>22</sup> B. Cavanagh, *J.*, 1927, 2207.

<sup>23</sup> F. L. Hahn and M. Frommer, *Z. physikal. Chem.*, 1927, **127**, 1; **A.**, 743.

<sup>24</sup> F. L. Hahn and G. Weiler, *Z. anal. Chem.*, 1926, **69**, 417; **A.**, 1927, 124.

<sup>25</sup> H. Brintzinger and F. Rodis, *Z. anorg. Chem.*, 1927, **166**, 53; **A.**, 1047.

<sup>26</sup> E. Zintl and G. Rienäcker, *ibid.*, 1927, **161**, 374; **A.**, 536.

<sup>27</sup> *Idem*, *ibid.*, p. 385; **A.**, 536.

<sup>28</sup> H. Brintzinger and F. Oschatz, *ibid.*, 1927, **165**, 221; **A.**, 953.

<sup>29</sup> E. Müller and H. Hentschel, *Z. anal. Chem.*, 1927, **72**, 1; **A.**, 1046.

<sup>30</sup> I. M. Kolthoff and J. J. Vleschhouwer, *Rec. trav. chim.*, 1926, **45**, 923; **A.**, 1927, 127.

Measurement in this way of the bivalent ion formed by reduced ferric iron with stannous chloride serves to evaluate the latter.<sup>31</sup> Ferrocyanide, not exceeding  $N/100$ -concentration, may also be titrated with bromate.<sup>30</sup> The reaction of iron and aluminium salts with sodium hydroxide has been followed potentiometrically;<sup>32</sup> in the case of aluminium, other bases have also been studied.<sup>33</sup>

The zinc-ferrocyanide titration has been studied<sup>34</sup> and applied to the determination of potassium by measuring the excess of calcium ferrocyanide over that required to precipitate the potassium from a solution containing 30% of alcohol.<sup>35</sup> Other investigations in this field include that of tungstic acid,<sup>36</sup> of certain of the noble metals with titanous chloride,<sup>37</sup> and of dichromate with ferrocyanide.<sup>38</sup>

J. J. Fox.

B. A. ELLIS.

<sup>31</sup> K. Sandved, *Analyst*, 1927, **52**, 2; **A.**, 127.

<sup>32</sup> P. Drossbach, *Z. anorg. Chem.*, 1927, **166**, 225; **A.**, 1047.

<sup>33</sup> F. O. Anderegg and G. W. Daubenspeck, *Proc. Indiana Acad. Sci.*, 1925, **35**, 141; **A.**, 1927, 640.

<sup>34</sup> G. G. Reissaus, *Z. anal. Chem.*, 1926, **69**, 450; **A.**, 1927, 126.

<sup>35</sup> A. Rauch, *Z. anorg. Chem.*, 1927, **160**, 77; **A.**, 331.

<sup>36</sup> H. T. S. Britton, *J.*, 1927, 147.

<sup>37</sup> W. D. Treadwell and M. Zürcher, *Helv. Chim. Acta*, 1927, **10**, 281; **A.**, 334.

<sup>38</sup> K. Someya, *Z. anorg. Chem.*, 1926, **159**, 158; **A.**, 1927, 224.

## BIOCHEMISTRY.

As in the past three years, this Report is written in two sections : plant, and animal biochemistry. The arrangement of the subject matter of the section dealing with the biochemistry of plants follows closely that adopted in the Report for 1926. Attention has been confined mainly to the biochemical and physiological aspects of the subject; the chemistry of soils and matters chiefly of agricultural chemical interest are discussed by the Reporter on "Soils and Fertilisers" in the Reports on Applied Chemistry. This arrangement brings these two Reports more or less into line with the apportionment of papers by the Bureau of Chemical Abstracts as between **A** and **B** Abstracts. There remain, however, certain agricultural problems concerned with the biochemistry of soils and with plant nutrition which seem to find their place naturally in this Report.

It has been possible to deal only with a limited number of divisions of the subject and those selected for treatment fall naturally into two main sections, one concerned with chemical changes accompanying the activities of the lower forms of plant life and the other with the biochemistry of the higher plants. Consideration of work on the chemistry of the humic matter of the soil has been omitted, since, although a number of papers have appeared, no great advance has been made and the subject has been very fully discussed in recent Reports.

In the period under review, the publication by E. C. C. Baly and his co-workers of the results of further work on the photosynthesis of naturally occurring compounds is of special importance. The announcement of their discovery of the mechanism of photosynthesis *in vitro* would appear to be a great step towards the understanding of this fundamental reaction as it occurs in nature and may be expected to lead to further rapid advances.

The early work of Mazé on the function of elements, other than the primary elements, in plant nutrition, and recent investigations on the importance of mineral elements in animal nutrition have stimulated the output of work on the inorganic constituents of plants and considerable progress with this subject has been made.

In considering the work of the year, a general impression is felt that an increasing amount of interest is being taken in the biochemistry of plants. Apart from its fundamental importance from

the purely scientific point of view, the subject is of the greatest economic consequence and its field includes investigations of value to many industries besides the primary industry of agriculture. Broadly speaking, the general aim of a century's work on plant nutrition has been the increase of the yield per acre—the quantity—of our agricultural crops, and, while that aim still remains, there is now coupled with it an increasing tendency to investigate the more difficult and elusive problems connected with quality. In this connexion, research in this country has received welcome aid from the Empire Marketing Board, and it is to be expected that further problems of this nature will be put forward for solution as an outcome of the recent Imperial Conference on Agricultural Research.

The writer of the section on plant biochemistry gratefully acknowledges the collaboration of Mr. H. J. G. Hines, B.Sc.

In regard to the section of this Report which deals with the biochemistry of animals the plan adopted is the same as that of the plant section, that is to say, only a limited number of subjects have been dealt with and these comprise fields of research in which noteworthy and co-ordinated advances have been effected. The main subjects reviewed are therefore: (1) the vitamins, in which theme special attention is directed to the differentiation of the components of the group of water-soluble *B*-vitamins, and to the formation of vitamin-*D* by irradiation processes; (2) the chemistry of the hexose phosphates and the rôle of these compounds and other organic phosphates in muscle; (3) the work of Meyerhof and his school on the lactic acid-forming enzymes isolated from mammalian muscle; (4) the developments of the past two years in the investigation of hæmoglobin and related compounds. The Reporter feels that it is necessary to adopt some such scheme of restrictions as that just outlined in order to present a reasonably homogeneous and readable account within the space at his disposal. At the same time, it is realised that consideration of many important papers published during the past year has been omitted. That is inevitable and in no sense is the omission to be interpreted as a judgment of inferiority in comparison with results which have been included in the matter of this Report. Again no attempt has been made to deal with isolated results in new or limited fields. It may be possible to deal with the latter category in future Reports when the lines of advance become more clearly demarcated.

#### *Micro-organisms.*

*Decomposition of Organic Matter.*—In last year's Report mention was made of the work of Waksman and Skinner,<sup>1</sup> who showed

<sup>1</sup> *Ann. Reports*, 1926, **23**, 213.

that both bacteria and fungi are concerned in the breakdown of celluloses in the soil. The investigations of S. Winogradsky<sup>2</sup> and of A. Kalnins<sup>3</sup> in this connexion have confirmed and extended the earlier work of Hutchinson and Clayton.<sup>4</sup> Both these workers have isolated new forms of bacteria from the soil capable of decomposing cellulose aerobically; the organisms studied by Winogradsky formed products resembling soil humus in being colloidal and nitrogenous, resistant to further bacterial attack, and soluble in dilute alkalis.

A careful study of the conditions attaching to the decomposition of cellulosic material has been made by R. D. Rege<sup>5</sup> in continuation of the work of Hutchinson and Richards.<sup>6</sup> The latter held the view that any cellulosic material containing 30% of pentosans and a relatively small amount of woody fibre would be readily decomposable by soil micro-organisms provided that a supply of available nitrogen and mineral nutrients was suitably incorporated with it. This has been confirmed by Rege's work, and it is shown that by using suitable analytical methods, the "decomposability" of any cellulosic material can be predicted. A study of the agents responsible for decomposition showed that three common species of soil fungi were particularly active in the decomposition of rice straw. Under aerobic conditions, these fungi, in combination, proved much more active than the soil bacteria alone. The optimum temperature for the growth of one of them, a species of *Acrimoniella*, lies between 40° and 50° and the maximum at about 60°, and, under the conditions obtaining in manure heaps, it is probable that the greater part of the decomposition is performed by fungi. In experiments with poplar wood, attempts were made to hasten decomposition by increasing the supply of energy material, carbohydrates being added to the wood for that purpose; the structural material remained, however, unattacked until the easily available material outside was exhausted. It will be seen that, in the main, the results of this investigation fall into line with the evidence accumulated in favour of the "lignin" hypothesis of the origin of humic matter in soil and with the views of Waksman referred to in the Reports for 1925 and 1926.<sup>7</sup> It has been shown by A. C. Thaysen and W. E. Bakes,<sup>8</sup> in a study of the early stages of decomposition of oat-straw by micro-organisms, that the pentosans of the raw

<sup>2</sup> *Compt. rend.*, 1926, **183**, 691; 1927, **184**, 493.

<sup>3</sup> *Ann. Report for 1925-26, Roth. Exp. Sta.*, 1927, p. 37.

<sup>4</sup> *J. Agric. Sci.*, 1919, **9**, 143; *Ann. Reports*, 1919, **16**, 174.

<sup>5</sup> *Ann. Appl. Biol.*, 1927, **14**, 1.

<sup>6</sup> *J. Ministry Agric.*, 1921, **28**, 398.

<sup>7</sup> *Ann. Reports*, 1925, **22**, 208; 1926, **23**, 211.

<sup>8</sup> *Biochem. J.*, 1927, **21**, 895.

material are at least partly responsible for the appearance of the carbohydrate fraction of the humus.

C. Barthel and W. Bengtsson<sup>9</sup> consider that, although in general the rate of decomposition of cellulose in plant material is directly proportional to the content of nitrogen, the slower decomposition of leguminous plants in the soil as compared with straw crops may be due to the higher content of non-cellulosic nitrogen-free material in the former. This may be of interest in connexion with the results obtained at the Woburn Experimental Farm in the permanent experiments on green manuring, where mustard has given much better results than vetches.

Our knowledge of the chemical and biological processes occurring in swamped and water-logged soils has hitherto been confined to scattered and isolated observations. In irrigated soils, more particularly those used for paddy rice, a water-logged condition is normal and it is not to be expected that the biochemical changes will be the same as those occurring in well-aërated soils. V. Subrahmanyam<sup>10</sup> has published the first portion of a systematic investigation of this question. In his first paper he deals with the influence of water-logging, under laboratory conditions, on the nitrogen compounds present, on the reaction, on gas production, and on bacterial numbers. The only prominent change in the nitrogen compounds is an increase in the amount of ammoniacal nitrogen, which results in a slightly more alkaline reaction. The absence of any appreciable production of carbon dioxide, and the lack of any marked increase in bacterial numbers, under aërobic or anaërobic conditions, suggested that the ammonia production was due to enzyme action. This hypothesis is confirmed by the work recorded in the second paper, in which it is shown that production of ammonia is not hindered by antiseptics and that an aqueous glycerol extract of the toluene-treated soil contains an agent which is able to produce ammonia from simple protein derivatives and from which an active preparation of a deaminase of a protein-like character was isolated. It is concluded that this enzymatic deamination may play an important part in plant nutrition in water-logged soils. It is perhaps worthy of note that the rice plant seems to thrive better when supplied with nitrogen in the form of ammonium salts than when fertilised with nitrates.

J. König<sup>11</sup> has studied the decomposition of farmyard manure and its utilisation by plants and arrives at conclusions which are

<sup>9</sup> *Kgl. Landbruks. Åhad. Handl. Tid.*, 1927, **66**, 306.

<sup>10</sup> *J. Agric. Sci.*, 1927, **17**, 429, 449.

<sup>11</sup> *Mitt. deut. Landw.-Ges.*, 1926, **552**, 571; **B.**, 1927, 198.

in close agreement with those of Bach referred to in last year's Report.<sup>12</sup> S. A. Waksman and F. G. Tenney<sup>13</sup> have begun a detailed investigation of the composition of natural organic materials and their decomposition in the soil.

In dealing with the organic matter of soils and manures, the publication of several papers on the action of hydrogen peroxide on organic matter should be mentioned. Following the method proposed by G. W. Robinson and Jones<sup>14</sup> for the determination of the degree of humification of soil organic matter, G. H. G. Jones<sup>15</sup> has attempted to determine the degree of humification of samples of farmyard manure by means of hydrogen peroxide and finds good correlation between the figures obtained and the degree of decomposition of the manure as judged by its appearance and history. W. O. Robinson,<sup>16</sup> in America, has also described a method for the determination of the organic matter of soils by digestion with hydrogen peroxide, but holds that hydrogen peroxide cannot be used to differentiate between humified and non-humified material and that, in the presence of soil, it does not determine any clearly defined type of organic matter. He further states that the method is not in any case applicable to soils high in calcium carbonate, manganese dioxide, or chromium sesquioxide; and in this connexion, the work of K. Scharrer<sup>17</sup> on the catalytic decomposition of hydrogen peroxide by soils is of interest. He found that the power to decompose hydrogen peroxide was much greater in neutral and alkaline soils than in acid soils, and that the greater the amount of manganese, iron or calcium in the soil the greater was its activity. Loss on ignition of soils involved loss of catalytic power only in so far as it reduced the content of carbonate and thereby the alkalinity of the soil. The soil containing the lowest number of bacteria had also the lowest catalytic power, but there was no direct relationship between bacterial numbers and activity.

*Production of Acids by Micro-fungi.*—The nutrition of micro-fungi and the chemical changes due to their activities have attracted a considerable amount of attention during the past two years, and, in the main, interest has centred in the production of acids, in particular citric and oxalic acids, from glucose and sucrose. The formation of citric and oxalic acids from sugars by *Aspergillus niger* has been confirmed by W. S. Butkewitsch,<sup>18</sup> who showed that

<sup>12</sup> *Ann. Reports*, 1926, **23**, 213.

<sup>13</sup> *Soil Sci.*, 1927, **24**, 275, 317.

<sup>14</sup> *J. Agric. Sci.*, 1925, **15**, 26; *B.*, 1925, 140.

<sup>15</sup> *Ibid.*, 1927, **17**, 104; *B.*, 232.

<sup>16</sup> *J. Agric. Res.*, 1927, **34**, 339; *B.*, 535.

<sup>17</sup> *Biochem. Z.*, 1927, **189**, 125; *B.*, 918.

<sup>18</sup> *Ibid.*, 1927, **182**, 99; *A.*, 382.

gluconic acid also was produced.<sup>19</sup> If calcium carbonate was present in the cultures or if nitrogenous compounds were absent, gluconic acid was formed in larger amounts than citric or oxalic acid. Under the same conditions, the mould *Mucor stolonifer* produced fumaric and oxalic acids only. Working on the fermentation of various carbohydrates by two separate strains of *A. niger*, H. Amelung<sup>20</sup> observed that one of the strains gave rise to citric and gluconic acids only, whereas the other formed oxalic acid in addition. Citric acid was obtained from compounds with three, five or six carbon atoms in the chain, but no acid was formed from four or seven carbon-atom chains (erythritol, glucoheptose). Gluconic acid was found only in cultures containing dextrose, sucrose, or maltose. It is considered doubtful whether gluconic acid is an intermediate stage in the fermentation of dextrose by these moulds.

F. Challenger and his associates<sup>21</sup> have made a systematic study of the mechanism of the formation of citric and oxalic acids from sugars by *A. niger*, investigating the fermentation of the various breakdown products in turn. When the mould is grown with citric acid as the sole source of carbon, the formation of malonic and glyoxylic acids can be detected; acetone is also formed, this being the first recorded instance of its production by a mould. It was suggested in the first paper by these authors that acetone-dicarboxylic acid was an intermediate stage in the formation of acetone and the actual occurrence of this compound was demonstrated later when ammonium citrate was employed instead of free citric acid as the source of carbon. Glyoxylic acid was obtained both from malonic acid and from calcium acetate, in the latter case calcium oxalate and glycollic acid also being formed. Franzen and Schmitt<sup>22</sup> have suggested that saccharic acid is an intermediate in the formation of citric acid in the higher plants; and that this view holds for its formation from glucose by *A. niger* is shown by the isolation of potassium hydrogen saccharate from cultures with glucose as the only source of carbon. Fermentation of calcium gluconate solutions gives rise to calcium saccharate and some citrate and, further, potassium citrate is formed in considerable amount when the mould is grown on potassium hydrogen saccharate solution. The formation of saccharic acid from glucose

<sup>19</sup> The formation of gluconic acid by other species of moulds has been investigated by T. Takahashi and T. Asai, *Proc. Imp. Acad. Tokyo*, 1927, **3**, 86; **A.**, 596; O. E. May, H. T. Herrick, C. Thom, and M. B. Church, *J. Biol. Chem.*, 1927, **75**, 417.

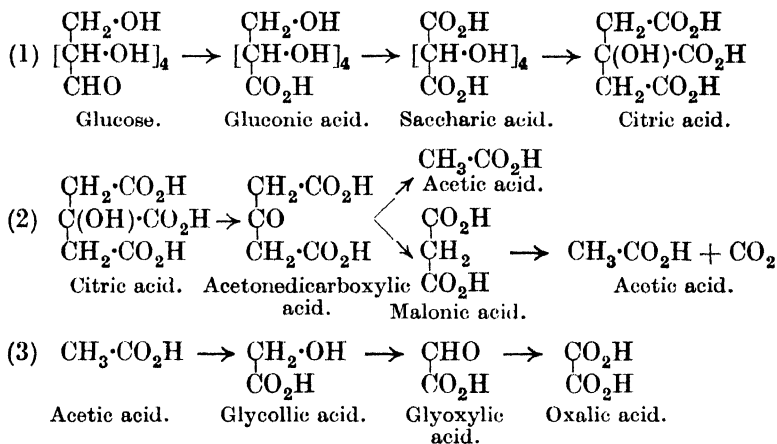
<sup>20</sup> *Z. physiol. Chem.*, 1927, **166**, 161; **A.**, 703.

<sup>21</sup> F. Challenger, V. Subramaniam, and T. K. Walker, *J.*, 1927, 200, 3044.

<sup>22</sup> *Ber.*, 1925, **58**, 222.



by certain yeasts<sup>23</sup> appears to be the only other case known in which this compound has been shown to be formed by micro-organisms. The demonstration of the importance of this acid in the mycological production of citric acid, and of acetonedicarboxylic acid in the further conversion of citric acid into oxalic acid, is of considerable biochemical significance. The results obtained by these authors lead to the suggestion that the mechanism of the formation of citric and oxalic acids by *A. niger* is as follows:—



Amelung<sup>24</sup> states that oxalic acid appears to be the universal product of incomplete oxidation of organic substances and may be produced by the breakdown of carbohydrates, proteins, fats, alcohols, and organic acids. Acid formation is unquestionably the result of processes taking place in the living cell and does not occur with dried preparations or with the expressed juice of fungi. The maximum action is attained at the optimum temperature for growth. The fact, noted above, that different strains of *A. niger* gave rise to different end products may prove to be of importance in the detection and classification of strains of the same species of fungi, a problem with which mycologists are much concerned at the present time.

L. K. Pearson and H. S. Raper<sup>25</sup> have shown that the fatty acids formed by *A. niger* and by *Rhizopus nigricans* vary with the temperature at which the organisms are grown. D. Chouchak<sup>26</sup> discusses the interesting question of the competition between the micro-organisms of the soil and higher plants for mineral nutrients;

<sup>23</sup> See Grüss, *Jahrb. wiss. Bot.*, 1926, **66**, 155, 171, 177.

<sup>24</sup> *Loc. cit.*, ref. 20.

<sup>25</sup> *Biochem. J.*, 1927, **21**, 875; *A.*, 906.

<sup>26</sup> *Compt. rend.*, 1927, **185**, 82.

and the calcium requirements of algæ and fungi are dealt with by Loew.<sup>27</sup> B. M. Bristol-Roach<sup>28</sup> has studied the carbon nutrition of some algæ isolated from soil and finds that all the species tested were capable of growth in complete darkness, provided that a suitable organic compound was present, but the requirements of individual species and their responses to different conditions were widely different. The respiratory and fermentative activities of a number of species of green algæ are discussed in an interesting paper by L. Genevois.<sup>29</sup> It is concluded that the "intramolecular" respiration of algæ is essentially similar to yeast fermentation. Some other papers on a number of points relating to the nutrition of different species of fungi are noted below.<sup>30</sup>

### *Higher Plants.*

*Photosynthesis.*—A distinct advance in our knowledge of the mechanism of the photosynthesis of naturally occurring compounds is marked by the appearance of three papers by E. C. C. Baly and his collaborators.<sup>31</sup> As the result of earlier work at Liverpool,<sup>32</sup> the opinion was expressed that photosynthesis of carbohydrates by the action of ultra-violet light on carbonic acid took place in two stages, involving, first, conversion of the carbonic acid molecule into activated formaldehyde and oxygen which then lost energy and appeared in their ordinary state, and, secondly, reactivation of the formaldehyde by light and its polymerisation to form reducing sugars. It is now held that it was unnecessary to have postulated two separate stages and that the activated formaldehyde produced from the carbonic acid can itself polymerise to reducing sugars without loss of energy and subsequent re-activation. According to this view, the small amounts of formaldehyde detected when ultra-violet light acts on aqueous solutions of carbonic acid are not due to its direct formation in the first stage, but to the secondary photochemical decomposition of the photosynthesised carbohydrates.

The earlier results obtained were criticised by C. W. Porter and

<sup>27</sup> *Biol. Zentralbl.*, 1927, **17**, 481.

<sup>28</sup> *Ann. Bot.*, 1927, **41**, 509; **A.**, 994.

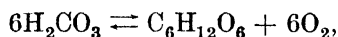
<sup>29</sup> *Biochem. Z.*, 1927, **186**, 461; **A.**, 905.

<sup>30</sup> M. Chikano and T. Kitano, *Z. physiol. Chem.*, 1927, **164**, 217; **A.**, 596; A. Rippel and H. Bortels, *Biochem. Z.*, 1927, **184**, 237; **A.**, 597; H. Tamiya, *Acta Phytochim.*, 1927, **3**, 51; **A.**, 906; Coupin, *Compt. rend.*, 1927, **184**, 1575; Bach, *ibid.*, p. 1578; A. Hée, *Bull. Soc. Chim. biol.*, 1927, **9**, 802; R. Meyer, *Z. Pflanz. Düng.*, 1926, **A**, **8**, 121; **A.**, 1927, 280.

<sup>31</sup> E. C. C. Baly, J. B. Davies, M. R. Johnson, and H. Shanassy, *Proc. Roy. Soc.*, 1927, **A**, **116**, 197; E. C. C. Baly, W. E. Stephen, and N. R. Hood, *ibid.*, p. 212; E. C. C. Baly and J. B. Davies, *ibid.*, p. 219; **A.**, 1040, 1041. See also E. C. C. Baly, *Ind. Eng. Chem.*, 1924, **16**, 1016.

<sup>32</sup> See *Ann. Reports*, 1922, **19**, 220; 1923, **20**, 220; 1924, **21**, 184.

H. C. Ramsperger,<sup>33</sup> who, taking extreme precautions in regard to the purity of their materials, reached the conclusion that in complete absence of all impurities no trace of formaldehyde was formed. This divergence of opinion now appears to be explained, since Baly and his associates have shown that the action of ultra-violet light on carbonic acid is to establish a photostationary state represented by



the amount of carbohydrate present in this equilibrium being very small. This being so, the presence of oxidisable impurities would cause the reaction to proceed from left to right with the formation of a definite amount of carbohydrate which would be photochemically decomposed to formaldehyde. The existence of this photostationary state was established by exposing carbonic acid to ultra-violet light in the presence of Feder's solution;<sup>34</sup> definite reduction then took place, showing the presence of substances of aldehydic nature. In complete absence of carbon dioxide there was no reduction. Hexoses were introduced as a component of the equilibrium on account of the work of J. C. Irvine and G. V. Francis,<sup>35</sup> who examined a photosynthesised sugar syrup obtained by exposure of formaldehyde to ultra-violet light and found that glucose is produced to the extent of about one-third of the total reducing compounds formed.

Attempts were then made to shift the equilibrium to the carbohydrate side by addition of a reducing agent to remove the oxygen, but without success, except in one case when rods of pure Swedish iron were used. The results obtained in these experiments, considered in connexion with the work of Zenghelis,<sup>36</sup> led to the investigation of the effect upon photosynthesis of carbohydrates of the introduction of a surface capable of adsorbing carbonic acid. Briefly stated, it was found that, whereas no measurable reaction takes place when pure carbonic acid in aqueous solution, free from all suspended matter, is exposed to light, a very definite action occurs when a surface which can adsorb the carbonic acid is present in the solution. Complex organic compounds, and not formaldehyde, are photosynthetically produced. These compounds char readily with sulphuric acid, and, after hydrolysis with hydrochloric acid, reduce Benedict's solution. If ammonium carbonate or barium or potassium nitrite was added, complex organic nitrogen compounds were formed. The following materials proved effective in providing

<sup>33</sup> *J. Amer. Chem. Soc.*, 1925, **47**, 79; *A.*, 1925, ii, 573.

<sup>34</sup> *Arch. Pharm.*, 1907, **245**, 25.

<sup>35</sup> *Ind. Eng. Chem.*, 1924, **16**, 1019; *Ann. Reports*, 1924, **21**, 186.

<sup>36</sup> *Compt. rend.*, 1920, **171**, 167.

a suitable surface: aluminium powder, barium sulphate, freshly precipitated aluminium hydroxide, and the basic carbonates of aluminium, zinc, and magnesium. Rigid precautions were taken and exhaustive tests carried out to ensure the complete absence of all organic matter in the carbon dioxide and other materials used. It was noted that aluminium hydroxide loses its efficacy in promoting photosynthesis after being in contact with water for some hours, and since the experimental details were identical when negative results were obtained with this material (the only variable factor being the nature of the surface), this offers further proof that the possibility of the positive results being due to the presence of organic impurities is excluded.

A further important step towards an explanation of photosynthesis of carbohydrates under natural conditions was achieved as the results of experiments with coloured powders in visible light. When the basic carbonate of nickel or of cobalt was used to provide a surface capable of adsorbing carbon dioxide, photosynthesised compounds similar to those described above were produced by exposure of the solutions to visible light only. Formaldehyde could not be detected, *i.e.*, the activated formaldehyde formed does not escape from the reaction sphere and become ordinary formaldehyde by loss of energy. Great care was again taken to ensure absence of impurities. The yield of organic material obtained was greater than when white powders and ultra-violet light were employed. One at least of the products was a carbohydrate which reduced Benedict's solution, gave the Molisch and Rubner reactions, and formed a solid osazone. There were also more complex substances which on hydrolysis reduced Benedict's solution. If ammonium bicarbonate was added, complex nitrogen compounds were formed, as in ultra-violet light. Photosynthesis of carbohydrates has thus been carried out in the laboratory using an exciting wave-length characteristic of natural photosynthesis.

The oxygen set free during the photosynthesis tends to poison the surface. Nickel or cobalt sesquioxide is formed as a film on the basic carbonate, and when the surface is completely poisoned, the carbohydrates previously formed tend to be photochemically decomposed under strong illumination. The surface slowly recovers itself under water.

In the third paper of the series, Baly and Davies discuss the question as to how far the photosynthesis achieved *in vitro* is similar to the process as it occurs in the living leaf. Whilst some of their suggested explanations of details are admittedly speculative, there is a close resemblance in many points. Ordinary formaldehyde does not take part in either case. In the laboratory, the process

has been realised by the action of light on carbonic acid adsorbed on a surface, and there is a considerable amount of evidence to show that a limiting surface exists in the chloroplasts of plants and is necessary for normal photosynthesis. Visible light and a visibly coloured surface are concerned in both processes. Fatigue effects are observed when the living leaf is exposed to too long and intense illumination, and when, in the laboratory, the surface becomes poisoned by oxygen.<sup>37</sup> There is a slow recovery in both cases and it appears that the photosynthesis must not proceed at a more rapid rate than this recovery process. The actual nature of the carbohydrates synthesised in the laboratory still remains to be ascertained.

Numerous attempts have been made by various investigators to isolate simple aldehydes from the leaves of plants, with a view to showing their existence as intermediate products in the process of assimilation.<sup>38</sup> It would seem probable from the work just discussed that such substances, if present in the leaf, are likely to be decomposition products rather than intermediates.

Some other recent work bearing on this subject may be considered in connexion with these interesting results. D. Burk<sup>39</sup> reports attempts to induce photochemical reactions between ammonia and various carbon compounds, including carbon dioxide, formic acid, formaldehyde, and dextrose. The solutions were contained in thin glass vessels and exposed to sunlight, various coloured catalysts being used. In some experiments, sunlight was condensed through lenses. No complex nitrogen compounds were produced from ammonia and carbonaceous substances, and with very few exceptions, no action of any sort was observed. It is significant that the exceptional cases when action was observed were those in which insoluble oxides were used as catalysts. When mercuric oxide was employed, formates, carbonates, nitrates, and nitrites were produced photochemically and the amounts formed seemed to be related to the extent of surface rather than to the bulk of the mercuric oxide used. Ammonia also gave rise to nitrites and nitrates in the presence of zinc oxide, but not when solutions of zinc salts were used. It is clear from the Liverpool work that the essential surface capable of adsorbing carbonic acid was lacking in most of Burk's experiments, and, further, that the excessive illumination employed, by inducing secondary photochemical decomposi-

<sup>37</sup> The probable formation of a peroxide is referred to; and it is of interest that H. Gaffron (*Ber.*, 1927, **60**, [B], 2229; **A.**, 1225) has recently shown that acceptor peroxides are produced during the photo-oxidation of aliphatic amines in the presence of chlorophyll.

<sup>38</sup> See *Ann. Reports*, 1926, **23**, 225.

<sup>39</sup> *J. Physical Chem.*, 1927, **31**, 1338; **A.**, 1040.

tion, would not be favourable to the detection of any complex products formed. A. K. Bhattacharya and N. R. Dhar<sup>40</sup> have found that finely divided zinc oxide acts as a sensitiser for many photochemical reactions, including the formation of carbohydrates from formaldehyde.

K. Noack<sup>41</sup> has studied the condition of chlorophyll in the living plant. Chlorophyll adsorbed from solution in light petroleum by means of dry colloidal aluminium hydroxide or dry lipin-free globin shows the red fluorescence characteristic of the chloroplasts of plants, and it appears that the red fluorescence is dependent on the existence of chlorophyll in the molecular disperse condition. In the living plant, chlorophyll is probably adsorbed on the proteins of the chloroplasts. The work of H. Gaffron<sup>42</sup> on oxygen transport by chlorophyll is also of interest. When chlorophyll is dissolved in acetone and exposed to light, it undergoes gradual oxidation, but if an oxygen acceptor is present, the chlorophyll is unchanged. It was shown that the ratio photochemical action/radiant energy adsorbed, as determined experimentally, was substantially the same as the value obtained from Einstein's law of photochemical equivalence on the assumption that one quantum of energy was used up for every molecule of oxygen utilised. This held true over a considerable range of wave-lengths, but was found to be dependent on the concentration of the oxygen acceptor.

#### *Carbohydrate Production and Transport.*

E. J. Maskell<sup>43</sup> has made observations on starch production in the potato, using a technique that made it possible to carry out the work in the field. By employing Sach's iodine test and a Ridgway colour scale, the net starch production was estimated as the difference between the colour value developed by a leaflet exposed to light on the plant for three hours and the colour value of the opposite leaflet which had remained covered. The observations were made on plants growing on plots which had received respectively potassium chloride, potassium sulphate, low-grade potash salts, and no potassium. Statistical analysis of the data showed that the rate of starch production was appreciably increased by potassium sulphate but not by the fertilisers containing chlorides. The rate of translocation of starch from the leaflets on the potassium sulphate plots was also increased, but this also varied significantly with other factors, of which intensity of solar radiation and age

<sup>40</sup> *J. Indian Chem. Soc.*, 1927, **4**, 298.

<sup>41</sup> *Biochem. Z.*, 1927, **183**, 135, 153; *A.*, 595.

<sup>42</sup> *Ber.*, 1927, **60**, [B], 755; *A.*, 428.

<sup>43</sup> *Ann. Bot.*, 1927, **41**, 237; *A.*, 704.

were important. The results were in the main borne out by manurial trials on the same land.

The seasonal changes in starch content in one- to five-year-old branches of bush-type apple trees have been followed by T. Swarbrick.<sup>44</sup> Starch disappearance tended to lag behind cambial activity in vegetative shoots, whereas the reverse was the case in flowering shoots.

It is maintained by Spengles and Wiedenhagen<sup>45</sup> that sugar is transported from the leaves to the roots of sugar-beet in the form of hexoses and not as sucrose, the latter being synthesised in the root.<sup>46</sup> A similar view of the processes occurring in *Canna edulis* is advanced by J. C. Ripperton,<sup>47</sup> who states that sucrose is formed in the leaves, and is transported through the stem in the form of invert sugar, resynthesis taking place in the root-stock with the formation of sucrose and starch.

#### *Leaf Cytoplasm.*

A. C. Chibnall and H. J. Channon<sup>48</sup> have made a study of the ether-soluble substances of the leaf cytoplasm of cabbage. Having worked out a method which enabled them to prepare these substances in bulk, they showed that the fraction obtained by adding acetone to the ethereal solution contained no phospholipins but that the main constituent was the calcium salt of a diglyceride-phosphoric acid to which the name of phosphatidic acid is assigned. The fraction not precipitated by acetone contained fatty acids which are not in combination with phosphorus compounds. The unsaturated acids, linolenic and linoleic acids, predominated; palmitic and stearic constituted the saturated acids; oleic acid was not definitely identified; arachidonic acid was absent. Hydrolysis of phosphatidic acid showed the presence of the same acids.

#### *The Nitrogenous Metabolism and Constituents of Plants.*

A series of papers dealing with the nitrogenous metabolism of apple trees has been published by W. Thomas.<sup>49</sup> The distribution of nitrogen in the water-soluble fraction of leaves and shoots was studied at intervals throughout a growing season, and in a subsequent season comparison was made between an unfertilised tree and one receiving a heavy dressing of sodium nitrate. Samples were

<sup>44</sup> *J. Pomology*, 1927, **6**, 137; *A.*, 797. See also E. L. Proebsting, *Hilgardia*, 1925, **1**, 81; *A.*, 1927, 488.

<sup>45</sup> *Z. Verein Deuts. Zuckerind.*, 1926, Lief. **842**, 767; *Bied. Zentralbl.*, 1927, **56**, 459; compare Davis, Daish, and Sawyer, *J. Agric. Sci.*, 1916, **7**, 225.

<sup>46</sup> See also H. Colin and R. Franquet, *Bull. Soc. Chim. biol.*, 1927, **9**, 114; *A.*, 599; H. Colin, *Compt. rend.*, 1927, **184**, 835; *A.*, 596.

<sup>47</sup> *Hawaii Exp. Sta. Bull.* **56**, 1927.

<sup>48</sup> *Biochem. J.*, 1927, **21**, 225, 233, 479, 1112; *A.*, 386, 799, 1227.

<sup>49</sup> *Plant Physiology*, 1927, **2**, 55, 67, 109, 245.

desiccated at 60° and, after suitable grinding, extracted with water. The separation of simple and conjugate proteins from their hydrolytic products was effected by means of colloidal ferric hydroxide. An examination of the nitrogen distribution in several different samples of residual material after extraction with water showed very consistent results, which in the opinion of T. B. Osborne indicated that a single protein is present, although the figures do not give absolute proof.

The detailed results of the investigation of the changes occurring throughout the year make interesting reading and work of this type will undoubtedly lead to clearer views of the changes occurring during the various periods of growth. When growth is rapid, nitrogen tends to migrate from the leaves to the shoots, where it is stored in the phloem. During bud formation, the reserve proteins are transported to the actively growing parts in the form of amino-acids. The phenomenon of autumnal migration of nitrogen from the leaves to the branches, a point of controversy with earlier investigators, is established and storage takes place mainly in the one- and two-year growths. Although the quantities, not only of soluble proteins, but also of the total water-soluble nitrogenous products, are small in *Pyrus malus* and make this species an unsuitable plant for investigation of the mechanism of protein synthesis, these results tend to confirm Chibnall's theory that amino-nitrogen is chiefly concerned in protein synthesis and "rest" nitrogen in protein degradation.<sup>50</sup> The results showed that nitrogen equilibrium of the whole tree would be just maintained by the application of 5 lb. of sodium nitrate.

In the following year's work, distinct differences in conformity with the fertiliser treatment were observed between two trees, one unmanured and the other receiving two heavy applications of sodium nitrate. The increased growth resulting from the treatment was reflected in the analyses, and the possible application of the results to horticultural practice has been dealt with in another paper.<sup>51</sup>

O. K. Stark<sup>52</sup> has carried out an investigation on the protein metabolism of the soya bean. Seedlings were grown under controlled conditions in darkness and determinations of amino-nitrogen were made at frequent intervals. In general, no correlation could be observed between period of growth and content of amino-nitrogen except in the very early periods; but since analyses were carried out on the whole plants, and not on the separate parts of

<sup>50</sup> *Ann. Reports*, 1924, **21**, 192.

<sup>51</sup> *Proc. Amer. Soc. Hort. Sci.*, 1926, 73.

<sup>52</sup> *Amer. J. Bot.*, 1927, **14**, 532.



the seedlings, this result is surely to be expected. The protein of the reserve material is broken down in one part and transferred to another; hence analyses of the whole plant will presumably give only equilibrium values at any particular time, except in the very early stages when little growth has occurred.

Among other papers on nitrogenous metabolism and nitrogen compounds in plants, the following may be briefly noted. C. O. Appleman and E. V. Miller<sup>53</sup> have investigated the changes in the nitrogen compounds in potatoes during growth and storage, the results failing to indicate any chemical or physiological basis for the superiority of immature potatoes for "seed." W. F. Gericke<sup>54</sup> has shown that the amount of nitrogen available at different stages of growth affects the protein content of wheat, the effects varying with different types of wheat. W. L. Davies<sup>55</sup> has given an account of the proteins of forage plants of the orders *Leguminosæ*, *Cruciferae*, and *Umbelliferae*, with analytical details. S. L. Jodidi<sup>56</sup> has compared the proteins of rice with those of other cereals, and has isolated asparagine from etiolated maize seedlings. C. G. Vinson<sup>57</sup> has studied the nitrogenous compounds extractable from maize pollen by dilute sodium hydroxide solution.

#### *Storage of Fruit.*

In addition to its purely scientific interest, the Report of the Food Investigation Board for the years 1925—26<sup>58</sup> illustrates the growing connexion that is being established between industry and biochemistry. The fruit trade suffers perhaps more than others from loss by wastage, and the preservation of perishable goods offers many interesting problems.

In this Report, investigations are described into the various factors favouring or preventing deterioration of fruit on storage, the work including both chemical studies on apples and pears of different varieties during ripening and storage and investigations into the suitability of various kinds of store.

The best-keeping varieties of apples are found to contain the least nitrogen and the most sugar and exhibit the lowest respiratory activity. Death ensues when the sugar is exhausted and this occurs the earlier if a large amount of protoplasm is present. Hence by a simple chemical determination the expectation of life of an apple during storage can easily be found.

The nature of the soil upon which the apples were grown had a

<sup>53</sup> *J. Agric. Res.*, 1926, **33**, 569; **B.**, 1927, 22.

<sup>54</sup> *Ibid.*, 1927, **35**, 133; **B.**, 826.

<sup>55</sup> *J. Agric. Sci.*, 1926, **16**, 280; **A.**, 1926, 761; *ibid.*, 1927, **17**, 33, 41; **B.**, 232.

<sup>56</sup> *J. Agric. Res.*, 1927, **34**, 309; **A.**, 800; *ibid.*, 1927, **34**, 649.

<sup>57</sup> *Ibid.*, 1927, **35**, 261; **A.**, 1227. <sup>58</sup> D.S.I.R., H.M. Stat. Office, 1927.

marked effect on the nitrogen content and hence on their keeping qualities. In general, specimens of the same variety from silt soil survived longer than those grown on gravel or fen soil at storage temperatures of 1° and 8°. At about the latter temperature, it was found possible to double the storage life by keeping the fruit in an atmosphere containing 9.2% of carbon dioxide and 11.8% of oxygen instead of air. Death of the fruit stored at 1° is accompanied by a browning of the tissue, a condition known as internal breakdown; in storage at 8° wastage is caused by a disease, "fungal rot," and not by internal breakdown. Slightly different results were obtained with pears, and indeed optimum storage conditions varied considerably amongst the several varieties.

Differences in the rates of respiration of different varieties of apples have been noted by B. D. Drain.<sup>59</sup> F. Gerhardt<sup>60</sup> also has investigated some of the changes involved in the ripening and storage of apples. He finds that the ripening process is accompanied by loss of moisture, acidity, dextrins, starch and acid-hydrolysable material, together with an increase in specific gravity, sugars, and soluble pectin. Only very slight chemical differences between normal tissues and those showing internal breakdown could be detected.

Work on the pectic substances of fruits has received attention in recent Reports,<sup>61</sup> and the subject continues to prove of interest. M. H. Carré and A. S. Horne<sup>62</sup> confirm earlier chemical investigations by a microscopical study of the tissues at various stages, and according to C. O. Appleman and C. M. Conrad<sup>63</sup> the transformation of protopectin into pectin appears to be the only pectic change associated with the ripening and softening of peaches. Other work on the chemistry of pectic substances is described by E. K. Nelson,<sup>64</sup> A. M. Emmett,<sup>65</sup> and by F. R. Davidson and J. J. Williamson.<sup>66</sup>

F. E. Denny<sup>67</sup> has published an interesting summary of his investigations on the curious effect of ethylene and other unsaturated hydrocarbons in producing colour changes and a break in the rest period of stored fruits and tubers. Other papers dealing with this subject are noted below.<sup>68</sup>

<sup>59</sup> *Bot. Gaz.*, 1926, **82**, 183.      <sup>60</sup> *Plant Physiology*, 1926, **1**, 251.

<sup>61</sup> *Ann. Reports*, 1925, **22**, 213; 1926, **23**, 228.

<sup>62</sup> *Ann. Bot.*, 1927, **41**, 193.      <sup>63</sup> *Maryland Agr. Exp. Sta. Bull.* 283, 1926.

<sup>64</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 2412, 2945.

<sup>65</sup> *Biochem. J.*, 1926, **20**, 564; **A.**, 1926, 872.

<sup>66</sup> *Bot. Gaz.*, 1927, **83**, 329.      <sup>67</sup> *Proc. Nat. Acad. Sci.*, 1927, **13**, 355.

<sup>68</sup> E. M. Chace and C. G. Church, *Ind. Eng. Chem.*, 1927, **19**, 1135; L. O. Regeimbal and R. B. Harvey, *J. Amer. Chem. Soc.*, 1927, **49**, 1117; **A.**, 599; L. O. Regeimbal, G. A. Vacha, and R. B. Harvey, *Plant Physiology*, 1927, **2**, 357; G. A. Vacha and R. B. Harvey, *ibid.*, p. 187.

*Structural Constituents of Plants.*

In last year's Report mention was made of current theories with regard to the origin of lignin and the work of M. H. O'Dwyer on the hemicelluloses of beechwood was referred to.<sup>69</sup> E. Schmidt and his collaborators<sup>70</sup> have been working for some years on the constitution of the structural components of plants and they consider that the cell-membrane of both archegoniates and phanerogams is made up of cellulose, hemicellulose, and incrustation. A cellulose-hemicellulose complex termed the "skeletal substance" is obtained by repeated treatment with chlorine dioxide and sodium sulphite alternately, incrustants and part of the hemicellulose being removed. The existence of two types of hemicellulose (compare O'Dwyer) is therefore postulated. Glycuronic acid occurs in the hydrolytic products of the hemicellulose of a number of plants differing widely in nature, including both archegoniates and phanerogams, thus indicating that, although the free acid is not present, a carboxylated polysaccharide, as its precursor, is common to both groups. An ester-like union of cellulose, glycuronic acid and hemicellulose is assumed to be present. Trustworthy figures for the determination of polyglycuronic acids were obtained by treatment of the skeletal substance with alkali hydroxide, followed by conductimetric titration with hydrochloric acid. W. Fuchs and E. Honsig<sup>71</sup> have criticised Schmidt's views on the ground that lignin obtained by the above treatment does not resemble lignins prepared in other ways. This would seem to be a fair criticism because of the drastic nature of the reagents employed. It is very improbable, however, that lignin has ever been isolated in the condition in which it exists in the plant, and, in this connexion, it may be noted that C. Dorée and E. C. Barton-Wright<sup>72</sup> have obtained a new type of alkali lignin by treating spruce dust with sodium hydroxide under pressure. This has been termed meta-lignin and is stated to agree in composition with the  $\alpha$ -lignin of Klason. A useful summary of present-day views on the origin and formation of plant-cell membranes from both the botanical and the chemical aspect of the subject has been published by van Iterson.<sup>73</sup>

*Absorption of Ions by Plants.*

In 1923, Robbins<sup>74</sup> advanced a theory explaining the differential absorption of ions by plants which was based on the isoelectric

<sup>69</sup> *Ann. Reports*, 1926, **23**, 231.

<sup>70</sup> E. Schmidt, F. Trefz, and H. Schnegg, *Ber.*, 1926, **59**, [B], 2635; *A.*, 1927, 80; E. Schmidt, K. Meinel, and E. Zintl, *ibid.*, 1927, **60**, [B], 503; *A.*, 383.

<sup>71</sup> *Ibid.*, 1926, **59**, [B], 2850.

<sup>72</sup> *Biochem. J.*, 1927, **21**, 290; *A.*, 597.

<sup>73</sup> *Chem. Weekblad*, 1927, **24**, 166.

<sup>74</sup> *Amer. J. Bot.*, 1923, **10**, 412; *Ann. Reports*, 1923, **20**, 226.

relations of the components of the living cells, particularly the proteins. If the acidity of the medium does not increase beyond the  $p_H$  represented by the isoelectric point of the cell colloids, most of the latter are on the electronegative side of their isoelectric points and therefore combine with an excess of basic over acid radicals. The medium increases in acidity, and hence some colloids pass over to the electropositive side, an absorption of anions resulting. J. Davidson <sup>75</sup> makes use of this hypothesis to explain the fact that relatively more potassium than phosphorus was absorbed by wheat seedlings grown in potassium phosphate solutions, irrespective of the initial hydrogen-ion concentration of the medium. Owing to buffer action, this preferential absorption did not result in any marked increase of acidity when the initial reaction was  $p_H$  6 or 7, but, with initial reactions of  $p_H$  5 or less, increased acidity was observed. At this lower  $p_H$  relatively more phosphorus was absorbed than at  $p_H$  6 or 7. It would thus appear that the physiological availability of phosphorus depends on the  $p_H$  value of the medium. In explaining absorption phenomena of this type, the author assumes that there is a relatively wide range in the isoelectric points of the individual protoplasmic ampholytes of the cells.

K. Lemanczyk <sup>76</sup> considers that absorption of potassium from nutrient solutions by the roots of barley consists of two phases, viz., equivalent absorption, including absorption of salt molecules as such, and ionic absorption. In the latter phase, to which the changes in the reaction of the solutions are due, potassium ions and anions in the solutions are exchanged respectively for calcium and magnesium ions and hydrogen carbonate ions in the root-cells.

The results of the experiments of A. R. C. Haas and H. S. Reed <sup>77</sup> on the absorption of ions by citrus and walnut seedlings are more difficult to understand. Citrus seedlings removed relatively more potassium than calcium from solutions containing approximately equivalent amounts of these ions. An interchange of ions was observed between the solutions and roots which resulted in an increased excretion of potassium in the solutions when the original concentration was low. Calcium ions were readily absorbed when sodium and potassium were absent or low in amount. With walnut seedlings, presence of excess of sodium chloride hindered absorption of calcium. More kations than anions were taken up from the solutions of single calcium salts by both citrus and walnut seedlings, causing an increase in acidity. The changes in reaction of the

<sup>75</sup> *J. Agric. Res.*, 1927, **35**, 335; **B.**, 950.

<sup>76</sup> *Bull. Acad. Polonaise*, 1926, **B**, 1109; **A.**, 1927, 1228.

<sup>77</sup> *Hilgardia*, 1926, **2**, 67; **A.**, 1927, 907.

culture solutions are attributed directly to differential absorption of ions, together with an excretion of certain ions. It appears that in complete nutrient solutions, citrus seedlings may in a comparatively short period bring about so great a concentration of hydrogen ions as to be injurious to the roots. In the view of these workers, "the absorption of ions is veiled by a host of factors, few of which are as yet understood," but they are of the general opinion that absorption is related to some chemical or physical property of the protoplasm. A purely physicochemical explanation is apt, however, to take little notice of chemical change and growth within the plant. Absorption is taking place, not in one cell only, but in chains of connected cells, and it is here perhaps that the explanation of some of the difficulties may be found.

In connexion with penetration into and absorption by living plant cells, Osterhout and his associates<sup>78</sup> have investigated the protoplasmic surfaces in the alga, *Valonia macrophysa*. The protoplasm forms a delicate layer, only a few microns in thickness, the two surfaces being alike as far as microscopic observation goes. By measurements of potential differences the conclusion is reached, however, that the protoplasm actually consists of three layers. Electrometric determinations on the chain sap-protoplasm-sap showed a potential difference of about 14.5 millivolts, the inner surface being positive with respect to the outer. The chain is assumed to be



where X is an outer, non-aqueous layer, W a middle aqueous layer, and Y an inner non-aqueous layer. The work of M. Irwin has been referred to in a previous Report.<sup>79</sup> She has continued her studies of the penetration of dyes into the vacuole of living cells of *Nitella* and *Valonia*,<sup>80</sup> investigating particularly the effects of acids, salts, and buffer mixtures on such penetration. The assumption of the existence of separate layers in the protoplasm proper is utilised to account for her results.

G. W. Scarth<sup>81</sup> also discusses the mechanism of the accumulation of dyes by living cells.

#### *Inorganic Constituents of Plants.*

A considerable volume of work has appeared in the last few years on the distribution and function of the inorganic constituents of

<sup>78</sup> W. J. V. Osterhout, E. B. Damon, and A. G. Jacques, *J. Gen. Physiol.*, 1927, **11**, 193.

<sup>79</sup> *Ann. Reports*, 1926, **23**, 224.

<sup>80</sup> *J. Gen. Physiol.*, 1926, **10**, 75, 271; 1927, **10**, 425, 927; 1927, **11**, 111, 123.

<sup>81</sup> *Plant Physiology*, 1926, **1**, 215.

plants, the subject being of special interest on account of the importance now attached by workers in animal nutrition to the mineral constituents of food rations. There is a tendency to take up problems of balance and correlation and emphasis is being laid on the relative quantities of the various elements present.

*Primary Nutrient Elements.*—O. Arrhenius<sup>82</sup> has published two papers dealing with experiments on the optimum concentrations of the primary nutrients for plant growth. He reaches the conclusion that in most soils the concentration of potassium is sufficient, whereas the concentration of phosphoric acid is about half that required for a favourable crop. The purpose of fertilising should be to alter the concentration of the nutritive substances to the optimum, and not necessarily to satisfy the demands of the plant.

Working with *Helianthus*, A. Rippel<sup>83</sup> has shown that the absorption of elements which are readily mobile in the plant, such as nitrogen, potassium, and phosphorus, accelerates the formation of dry matter, whereas less mobile elements such as calcium, magnesium, sulphur, and silicon have little or no effect. It is suggested that there is a relatively greater uptake of mobile elements during the earlier stages of growth of the plant.<sup>84</sup>

J. Davidson<sup>85</sup> has investigated the changes in nitrogen, potassium, and phosphorus during the germination and early stages of growth of wheat seedlings and finds that they may either lose or gain potassium and nitrogen, according to age and conditions, but that the content of phosphorus remains approximately constant. In an interesting paper, K. Maiwald<sup>86</sup> discusses the influence of large amounts of potassium and chlorine on the growth and leaf colour of potatoes. He found that excess of potassium or sodium ions alone effected a reduction in leaf colour, as compared with normal plants, of about 25%, chlorine ions alone about 70% and potassium and chlorine ions together about 60%. It was clear that with calcium chloride the effects were due solely to the chlorine ions and that with potassium and sodium sulphates the influence of the cations predominated. The author considers that, not only reduction in chlorophyll content, but many other phenomena concerned with plant metabolism, can be attributed to the alteration of the equilibrium between physiologically important ions.

J. H. MacGillivray<sup>87</sup> has shown that in phosphorus-starved

<sup>82</sup> Medd. Centralanstalt för forskvasendet jordbruks, 1927, Nos. 40, 41.

<sup>83</sup> Biochem. Z., 1927, 187, 272; A., 1116.

<sup>84</sup> On the influence of fertilisers on absorption of plant nutrients and formation of dry matter, see W. Schleusener, Z. Pflanz. Düng., 1926, A, 7, 137; B., 1927, 55.

<sup>85</sup> Bot. Gaz., 1926, 81, 87.

<sup>86</sup> Z. Pflanz. Düng., 1927, A, 9, 57; B., 565.

<sup>87</sup> J. Agric. Res., 1927, 34, 97; A., 599.

tomato plants there is a re-utilisation of the phosphorus present; about half the total amount is found in the fruit, irrespective of treatment, although, if there is a shortage of phosphorus, the size and number of the fruits are much decreased. There is an increase in the percentage of total nitrogen and of sugars present. The effects of deficient amounts of potassium, calcium, and magnesium on various plants have been studied by R. C. Burrell.<sup>88</sup>

The occurrence and distribution of sodium in plants and the ratio of the amounts of sodium and potassium present have been the subjects of several papers.<sup>89</sup> By comparing the composition of the seed with that of barley plants grown in darkness, with and without sodium and potassium, to the point of exhaustion of the reserve materials, A. Bobrownicka-Odrzywolska<sup>90</sup> has shown that in presence of potassium a smaller amount of carbohydrate is required for the formation of a unit of cellulose. Sodium has a similar effect if accompanied by other necessary mineral salts. Potassium also reduces the loss of organic matter and the percentage of starch decomposed for respiration purposes. The young plants made poorer growth in pure potassium or sodium chloride solutions than in distilled water; none the less, a smaller percentage of starch was decomposed for respiration. The translocation of potassium from leaves of ivy and poplar has been followed by T. Sabalitschka and A. Weise.<sup>91</sup>

*Secondary Elements in Plant Nutrition.*—The appearance of further papers asserting the indispensability to plants of certain elements hitherto neglected in this connexion would seem to involve reconsideration of what were regarded as established facts in plant nutrition. The pioneering work of Mazé<sup>92</sup> indicated the possibility that, by more refined methods, the ten elements postulated by Knop and the older physiologists as satisfying all the requirements of plant growth might be shown to be insufficient. These experiments, coupled with the stimulus due to the brilliant work on deficiency diseases which has demonstrated the importance of minute amounts of vitamins, hormones, and mineral elements in the animal body, have led to a number of investigations on the rôle of secondary elements in plant growth.<sup>93</sup>

<sup>88</sup> *Bot. Gaz.*, 1926, **82**, 320; **A.**, 1927, 596.

<sup>89</sup> G. Bertrand and J. Perietzeanu, *Compt. rend.*, 1927, **184**, 645, 1616; *Bull. Soc. chim.*, 1927, **41**, 709; **A.**, 488, 704, 1116; G. André and E. Demoussy, *Compt. rend.*, 1927, **184**, 1501; **A.**, 798.

<sup>90</sup> *Bull. Acad. Polonaise*, 1925, **B**, 801; **A.**, 1927, 384.

<sup>91</sup> *Z. Pflanz. Düng.*, 1926, **A**, 7, 166; **B.**, 1927, 55.

<sup>92</sup> *Ann. Reports*, 1916, **12**, 231.

<sup>93</sup> Earlier papers are referred to in *Ann. Reports*, 1922, **19**, 225; 1923, **20**, 219; 1925, **22**, 210.

The general line of the experiments now under notice is to attempt to grow plants in the usual nutrient solutions, prepared from highly purified chemicals, so that contamination with other elements is reduced to a minimum. Under these conditions, many plants fail to grow. The addition of very small traces of certain elements—boron, zinc, silicon, aluminium, manganese—has, in a number of instances, secured normal growth of the plants and all the above-named elements have been stated by different workers to be indispensable for proper growth.

In regard to boron, the earlier work of Miss Warington had shown that certain leguminous plants, but not barley and other cereals, could not be grown to maturity in solutions free from this element. Following up these observations, W. E. Brenchley and K. Warington<sup>94</sup> have attempted to replace boron for plants which require it by other elements, particular attention being paid to manganese; but, of 52 elements tested, none proved capable of so doing. On the other hand, G. H. Collings<sup>95</sup> states that, contrary to Miss Warington's findings, boron is not essential for the growth of the soya bean, although in water cultures a stimulating influence was observed. A. L. Sommer and C. B. Lipman,<sup>96</sup> taking elaborate precautions to purify all the materials used, have demonstrated that both boron and zinc are indispensable to many leguminous and non-leguminous plants, barley (see above) requiring both these elements. They are of the opinion that the explanation put forward by Brenchley and Thornton in 1925,<sup>97</sup> that the failure of legumes to grow in absence of boron is closely connected with injury to the nodule bacteria and consequent disturbance of the nitrogen metabolism of the plant, avoids the main issue.

A. L. Sommer<sup>98</sup> records experiments showing that small traces of aluminium and silicon are also necessary for normal growth; and J. S. McHargue, from analyses of cotton<sup>99</sup> and blue-grass,<sup>1</sup> concludes that manganese, copper, zinc, nickel, and cobalt may all be essential elements. Lack of manganese has been shown to be the cause of chlorosis in one instance,<sup>2</sup> and Bortels states<sup>3</sup> that zinc is necessary for the growth of the mould *Aspergillus niger*.

J. Stoklasa and his associates have for some time past concerned

<sup>94</sup> *Ann. Bot.*, 1927, **41**, 167; **A.**, 385.

<sup>95</sup> *Soil Sci.*, 1927, **23**, 83; **B.**, 307.

<sup>96</sup> *Plant Physiology*, 1926, **1**, 231.

<sup>97</sup> *Proc. Roy. Soc.*, 1925, **B**, **98**, 373; *Ann. Reports*, 1925, **22**, 210.

<sup>98</sup> *Univ. Calif. Pub. Agr. Sci.*, 1926, **5**, 57.

<sup>99</sup> *J. Amer. Soc. Agron.*, 1926, **18**, 1076; **A.**, 1927, 599.

<sup>1</sup> *Ind. Eng. Chem.*, 1927, **19**, 274; **B.**, 394.

<sup>2</sup> B. E. Gilbert, F. T. McLean, and L. J. Hardin, *Soil Sci.*, 1926, **22**, 437; **B.**, 1927, 171.

<sup>3</sup> *Biochem. Z.*, 1927, **182**, 301; **A.**, 485.



themselves with the occurrence of iodine in plants and the distribution of this element in the earth's crust. Their views are summarised in a recent paper,<sup>4</sup> in which it is pointed out that the presence of iodine can be detected both in volcanic rocks and in more recent rocks containing the fossilised remains of animal or plant life. They state that iodine promotes the growth of nitrifying bacteria and that the simultaneous presence of iodine and iron in the soil leads to a general enhancement of fertility; indeed, they regard iodine as an essential biogenic element in the synthesising processes of living cells. In this they are supported by K. Scharrer and his co-workers,<sup>5</sup> who show that iodides, iodates, and periodates materially increase the rate of reproduction of yeast, although without increasing the final maximum figure. Although these and other experiments make a strong case for the consideration of iodine as an important element in the economy of plants, there is evidence that conflicts with this view<sup>6</sup> and the claims put forward cannot be completely accepted until further confirmation is forthcoming.

It will be seen from this short summary that an interesting position has been reached. The work on "secondary" elements is still in an early stage and it is not surprising that somewhat conflicting results have been obtained by investigators working under different conditions. Experimental demonstration is difficult owing to the minute amounts involved, and conditions for growth in different parts of the world vary widely. Some plants may have a sufficient reserve of "secondary" elements in their seeds to carry them through a growing season, and therefore it is difficult to produce rigid proof of the essential nature of these elements; but it is probable that some, if not all, of the elements cited are necessary for the full and proper growth of different species of plants under different conditions.

Some clue as to the function of such elements is given by Brenchley and Warington,<sup>7</sup> who observed that boron appears to be associated with absorption or utilisation of calcium, possibly somewhat as silicon appears to be associated with phosphorus nutrition. The inter-relations between silicon and phosphorus form the subject of a paper by W. E. Brenchley, E. J. Maskell, and K. Warington,<sup>8</sup> whose results are on the whole in agreement with those

<sup>4</sup> *Z. angew. Chem.*, 1927, **40**, 20; **A.**, 171.

<sup>5</sup> K. Scharrer and J. Schwaibold, *Biochem. Z.*, 1927, **185**, 405; **A.**, 798; K. Scharrer and W. Schwartz, *ibid.*, 1927, **187**, 159; **A.**, 903. See also K. Scharrer, *Fortschr. Landw.*, 1927, **2**, 119, 249.

<sup>6</sup> See, e.g., W. E. Brenchley, *Ann. Applied Biol.*, 1924, **11**, 86.

<sup>7</sup> *Loc. cit.*

<sup>8</sup> *Ann. Applied Biol.*, 1927, **14**, 45.

reported previously.<sup>9</sup> From statistical examination of the data from pot experiments, they conclude that the effect of added silicate can be formulated in terms of an increase in the efficiency of the phosphoric acid present.

A valuable review of the literature regarding the effect on plants of copper, zinc, arsenic, boron, and manganese is given by Miss Brenchley in a recent publication.<sup>10</sup>

#### *General Changes with Growth.*

An investigation of agricultural and biochemical interest has been published by H. E. Woodman, D. L. Blunt, and J. Stewart<sup>11</sup> dealing with the seasonal variations in the productivity, botanical and chemical composition, and nutritive value of medium pasturage, both on light and on heavy soils. During late years, increasing interest has been shown in our pasture lands, and although experience and shrewd observation had led to the evolution of such systems of grazing as the "Hohenheim system,"<sup>12</sup> definite information of a chemical and botanical nature on the above factors was lacking. By far the greater part of the work done on the nutritive value of grassland has concerned itself with the hay crop, and little was known of the chemistry of the immature growth which obtains under grazing conditions. In the investigations now being considered, an attempt has been made to imitate close grazing by cutting plots at frequent intervals with a lawn mower. The produce so obtained was subjected to botanical and chemical analysis, and, in addition, digestibility trials were carried out.

It was found that, under these conditions, the grass contains a very high percentage of protein throughout the whole season, and the percentage of fibre is much lower than in meadow hay. The herbage in fact closely resembles a concentrated food, like linseed cake, that has been "watered down" and it has a much higher nutritive value than had previously been supposed. Unlike many farm concentrates, pasture grass is well supplied with vitamins and is also rich in bone-forming minerals. The experiments of 1925 on light land were repeated on heavy land in 1926 with substantially the same results, and the authors make the interesting suggestion that a future development may be the production of home-grown concentrates for winter maintenance simply by drying or ensiling short grass cuttings. E. J. Sheehy<sup>13</sup> found that the botanical composition and the nutritive value of the herbage of

<sup>9</sup> See *Ann. Reports*, 1925, **22**, 210.

<sup>10</sup> "Inorganic Plant Poisons and Stimulants," Camb. Univ. Press, 1927.

<sup>11</sup> *J. Agric. Sci.*, 1926, **16**, 205; 1927, **17**, 209; **B.**, 1926, 506; 1927, 588.

<sup>12</sup> *Ann. Reports Applied Chem.*, 1926, **11**, 462.

<sup>13</sup> *Sci. Proc. Roy. Dub. Soc.*, 1927, **18**, 389; **B.**, 791.

two pastures of different reputation could be correlated with the dry matter content of the grass.

Several investigations dealing with chemical changes during the growth of fruit may be noted here. R. H. Roberts<sup>14</sup> states that blossom bud formation in apples accompanies a condition of balance between the nitrogen and carbohydrate content; and G. T. Nightingale<sup>15</sup> has shown the importance of the same balance in determining the growth of tomato plants under conditions of long and of short illumination. The physical and chemical changes occurring during the ripening of grapes have been studied by P. R. v. D. R. Copeman and G. Frater.<sup>16</sup>

### *Biochemistry of Animals.*

#### *Vitamins.*

This year's work in the field of vitamins has been characterised by increasing activity and much important information has been added to that of preceding years. Although recent developments have not yet resulted in the isolation of any of the vitamins in what can be asserted with confidence to be a state of purity, there are several indications that this advance cannot be long delayed.

*Vitamin-A.*—Two publications have appeared from Japan by the workers who are continuing there the investigations commenced by the late Dr. Takahashi, and these appear to the Reporter to call for some comment. It was previously stated<sup>1</sup> that the preparation made from the unsaponifiable fraction of cod-liver oil, to which the formula  $C_{27}H_{42}(OH)_2$  was ascribed and which was called "biosterin," constituted essentially the pure vitamin. Very similar preparations had been obtained by Drummond and his co-workers<sup>2</sup> and an examination of these led to the conclusion that they were essentially unsaturated complex alcohols and hydrocarbons with which the vitamin was admixed in unknown but probably small amount. Nakamiya and Kawakami have now made a study of the hydrogenation products of "biosterin," and in a publication entitled "Hydrogenation of Sterol-free Unsaponifiable Matters of Cod-Liver Oil"<sup>3</sup> they describe the isolation from hydrogenated "crude biosterin" of nonacosane, batyl alcohol, myricyl alcohol, an unknown saturated alcohol of m. p. 89—91°, and octadecyl palmitate. Further, cholesterol appears to have

<sup>14</sup> *Wisconsin Agr. Exp. Sta. Res. Bull.* **68**, 1926; **A.**, 1927, 283.

<sup>15</sup> *Ibid.*, *Bull.* **74**, 1927; **A.**, 1225.

<sup>16</sup> *Dep. Agr. Union S. Afr. Sci. Bull.* **50**, 1926; **A.**, 1927, 908.

<sup>1</sup> *Ann. Reports*, 1925, **22**, 219.

<sup>2</sup> *Ibid.*, p. 219.

<sup>3</sup> *Sci. Papers, Inst. Phys. Chem. Research (Japan)*, 1927, **3**, 62.

been isolated from the unhydrogenated "crude biosterin" when the latter was subjected to further purification. In a second publication, "On the Hydrogenation of Biosterin"<sup>4</sup> the isolation of the same products is described from a preparation called "purified biosterin." In view of these results, it is a little difficult to understand why the terms "unsaponifiable" and "sterol-free" are used at all in the title of the first paper, and it would appear more than probable that in "biosterin" the Japanese workers are handling the same fraction of unsaturated alcohols and hydrocarbons as that studied by Drummond and his associates. The Reporter has thought it necessary to refer to these observations, since they would seem to dispose of the view, advanced with much circumstantial evidence, that "biosterin" really constituted vitamin-A, and they illustrate afresh the great technical difficulties which beset attempts to separate the vitamin in a pure state. Nakamiya and Kawakami confirmed the observation that the growth-promoting power of their fractions was completely lost after hydrogenation.

Rosenheim and Webster,<sup>5</sup> as the result of a large series of both colorimetric and biological tests, have found that the amount of vitamin-A present in liver fats other than that of the cod, in many cases far exceeds that present in the latter source. They state that the liver oils of fishes such as the salmon and halibut are often 100 times as rich in the vitamin as that of the cod. A discovery of much greater potential industrial importance is that the liver oils of herbivorous mammals, such as the sheep, calf, and ox, usually contain some ten times the concentration of the vitamin found in cod-liver oil. It is suggested that such mammalian oils, being free from the highly flavoured clupanodonic acid characteristic of fish oils, and from the chromogen responsible for the non-specific Fearon colour reaction,<sup>6</sup> are well suited for incorporation with margarine and so constitute a ready means of raising the latter to the same standard of biological efficiency as butter, so far as vitamin-A is concerned. There is, in fact, no reason why a higher standard should not be attained. Using the antimony trichloride test, Wilson<sup>7</sup> has found that the human liver has the same high content of vitamin-A as the livers of other mammals. Although the amount is rather variable, fatty extracts from human liver may contain as much as 25 times the amount found in cod-liver oil.

The mechanism of the arsenic or antimony trichloride colour reaction for vitamin-A still remains obscure. Rosenheim<sup>8</sup> has

<sup>4</sup> *Sci. Papers, Inst. Phys. Chem. Research (Japan)*, 1927, **7**, 121.

<sup>5</sup> *Nature*, 1927, **120**, 440; *Biochem. J.*, 1927, **21**, 111; *A.*, 271.

<sup>6</sup> Rosenheim and Webster, *Biochem. J.*, 1926, **20**, 1342; *A.*, 78; Willimott, Moore and Wokes, *ibid.*, p. 1292; *A.*, 78.

<sup>7</sup> *Biochem. J.*, 1927, **21**, 1054; *A.*, 1223.

<sup>8</sup> *Ibid.*, p. 386; *A.*, 486.

attempted to elucidate this question in a study of the chromogenic substance produced when a chloroform solution of cholesterol and benzoyl peroxide is evaporated to dryness. The substance obtained gives with arsenic trichloride a blue colour indistinguishable in appearance from that given by an oil containing vitamin-*A*. But when the purified chromogen is added to vegetable oils which do not themselves give the arsenic chloride reaction, no colour is then obtained. The colour developed by the artificial product does not fade so rapidly as that given by an oil containing the vitamin. Further, there are differences in the absorption spectra of the two pigments, and it is evident that this artificial chromogen, although it must bear some family resemblance to the natural chromogen or vitamin, is not identical with the latter. All the available evidence still supports the view that the chromogen and vitamin-*A* are one and the same substance.

In a study of the determination of vitamin-*A* by the biological method, Steenbock and Coward<sup>9</sup> recommend supplying vitamin-*D* in the form of an irradiated sterol, and state that the incidence of ophthalmia in experimental animals forms a better criterion of the depletion of the animal's store of vitamin-*A* than does cessation of growth.

*Vitamin-B*.—The past year has seen the definite recognition of what has been widely suspected by workers on this vitamin, namely, the existence of two distinct components of what has hitherto been called water-soluble vitamin-*B*. The question of nomenclature at once arises and the present occasion seems to be a suitable one for considering the general principles to be adopted in naming new vitamins—a problem which shows signs of becoming increasingly acute. For the worker in fields other than that of the vitamins, and for the medical practitioner, it must be highly disconcerting to find a vitamin, familiar to him under the term, shall we say, *X*, becoming fragmented into two or more vitamins *X*, *Y*, and *Z*, amongst which are distributed, in a manner quite mysterious to him, the properties formerly exclusively assigned to the original *X*. With the view of preserving a greater degree of continuity in the literature, it seems desirable to evolve a system which will obviate this difficulty and at the same time clearly differentiate the constituents of any complex vitamin group. For these reasons, it does not seem that the suggestions of Sherman and Axtmayer<sup>10</sup> are to be recommended. These are that the term "vitamin-*B*" be replaced by the terms "vitamin-*F*" (heat-labile, anti-neuritic component) and "vitamin-*G*" (heat-stable, pellagra-preventive

<sup>9</sup> *J. Biol. Chem.*, 1927, **72**, 765; **A.**, 595.

<sup>10</sup> *Ibid.*, 1927, **75**, 207; **A.**, 1223.

component). A recent suggestion of the Accessory Food Factors Committee<sup>11</sup> in this country seems more serviceable, and is to the following effect: (1) the term "vitamin-*B*" should be retained for the group of water-soluble vitamins to which the term was first applied by McCollum and Davis in 1915; (2) the term "vitamin-*B*<sub>1</sub>" should be used for the more heat-labile, anti-neuritic vitamin (called "torulin" by Kinnersley and Peters)<sup>12</sup> required to prevent polyneuritis in birds, marasmus, with or without paralysis, in mammals, and beri-beri in man; (3) the term "vitamin-*B*<sub>2</sub>" should be given to the more heat-stable component (called *P-P* by Goldberger and his associates in America) necessary for the maintenance of growth and health, and for the prevention of characteristic skin lesions in rats and of pellagra in man. The committee also recommend that the term "bios" be retained for the substance or substances encouraging the rapid growth of yeast-cells. These suggestions are only tentative and have not as yet been officially adopted; nevertheless for the sake of simplicity and clarity the use of the terms *B*<sub>1</sub> and *B*<sub>2</sub> will be adopted in this Report.

Since the adoption of the view that the growth-promoting, water-soluble vitamin-*B* was identical with the anti-neuritic vitamin curative of polyneuritis in birds—a suggestion first made by McCollum and Kennedy in 1916—much evidence has accumulated which is slightly but definitely at variance with that view, and it is the steady accretion and strengthening of this evidence which has led to the recommendations mentioned above. The evidence against the identity of water-soluble-*B* (in the original strict sense) with the anti-neuritic vitamin may be grouped under three heads: <sup>13</sup> (1) distribution in nature; (2) differences in heat stability; (3) differences in solubility and other physical properties. As regards (1), wheat embryo is rich in *B*<sub>1</sub> but poor in *B*<sub>2</sub>, whereas the reverse is true of milk, meat, green leaves, roots and tubers. Many yeasts of equal *B*<sub>2</sub> content vary considerably in regard to *B*<sub>1</sub>. Under (2) come the observations that at 120° *B*<sub>1</sub> is much more sensitive to inactivation than is *B*<sub>2</sub>, so that on autoclaving yeast for four or five hours there is obtained a preparation devoid of *B*<sub>1</sub> but still potent as regards *B*<sub>2</sub>. (3) The physical differences are shown by the greater solubility of *B*<sub>1</sub> in alcohol, acetone, and benzene, and further by the greater tendency of *B*<sub>2</sub> to be adsorbed by charcoal or fuller's earth.

<sup>11</sup> Appointed jointly by the Medical Research Council and the Lister Institute of Preventive Medicine.

<sup>12</sup> *Biochem. J.*, 1925, **19**, 820; 1927, **21**, 777; *A.*, 1925, i, 1516; *A.*, 1927, 904.

<sup>13</sup> Chick and Roscoe, *Biochem. J.*, 1927, **21**, 698; *A.*, 702; Sherman and Axtmayer, *loc. cit.*; Salmon, *J. Biol. Chem.*, 1927, **73**, 483; *A.*, 796.

The studies of human pellagra by Goldberger and his associates <sup>14</sup> dating from 1924 have led to the abandonment of their earlier theory that this disorder was caused by the inferior biological value of the dietary proteins, and to the adoption of the view that there is present in water-soluble vitamin-*B* a pellagra-preventive principle (which they call *P-P*), identical with the growth-promoting principle of McCollum and Davis. Chick and Roscoe <sup>15</sup> corroborate the results of Goldberger in regard to pellagra. Important further support of these views regarding the multiple nature and physiological rôle of the components of vitamin-*B* is forthcoming from Drummond's laboratory,<sup>16</sup> and it would appear that much conflicting evidence regarding the physiological rôle of vitamin-*B* will become more easily interpreted on wider recognition of its composite nature. That the complexity of vitamin-*B* may not have been completely unfolded by the recognition of vitamins-*B*<sub>1</sub> and -*B*<sub>2</sub> is suggested by the observation of Boas <sup>17</sup> that crude egg-white, boiled and supplemented by an adequate diet, is not capable of supporting growth and health in young rats if the egg-white has been dried before being boiled. On the other hand the efficiency of the egg-white is not impaired if it be coagulated previous to desiccation. The ill-effects resulting from the ingestion of dried egg-white are counteracted by raw potato, potato starch, arrowroot, dried yeast, fresh egg-white, egg-yolk, milk, commercial casein, crude lactalbumin, spinach, cabbage leaves, banana, and dried horse serum. These substances are supposed to possess some protective principle which, although similar in distribution to the *B*-vitamins, is not identified with either *B*<sub>1</sub> or *B*<sub>2</sub>. It is further suggested that there is a balance between the amount of the dried egg-white ingested and the amount of the protective principle required. A somewhat similar problem was encountered by Reader and Drummond,<sup>18</sup> who found that a diet consisting largely of casein became adequate when the ratio of yeast extract to protein was raised considerably, and related problems of balance of food-stuff by vitamin-*B* have been investigated by Plimmer, Rosedale, and Raymond.<sup>19</sup>

The isolation of vitamin-*B*<sub>1</sub> is claimed by Jansen and Donath,<sup>20</sup>

<sup>14</sup> Goldberger and Tanner, *U.S. Pub. Health Rep.*, 1924, **39**, 87; 1925, **40**, 54; Goldberger, Wheeler, Lillie, and Rogers, *ibid.*, 1926, **41**, 297; Goldberger and Lillie, *ibid.*, p. 1025.

<sup>15</sup> *Loc. cit.*

<sup>16</sup> Kon and Drummond, *Biochem. J.*, 1927, **21**, 632; Hassan and Drummond, *ibid.*, p. 653; **A.**, 702.

<sup>17</sup> *Ibid.*, 1927, **21**, 712; **A.**, 797.

<sup>18</sup> *Ibid.*, 1926, **20**, 1256; **A.**, 1927, 79.

<sup>19</sup> *Ibid.*, 1927, **21**, 913, 1141; **A.**, 905, 1224.

<sup>20</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1390; **A.**, 1927, 382.

who describe the isolation of a residue weighing 1.4 g. from 100 kg. of rice polishings and containing about one-quarter of the amount of the vitamin originally present. The product is stated to be the hydrochloride of a base and to it the formula  $C_6H_{10}ON_2 \cdot HCl$  is ascribed. Its chemical behaviour suggests the presence of a glyoxaline nucleus. Eykman<sup>21</sup> states that this preparation cures polyneuritis in fowls.

*Vitamin-C.*—No very striking advance falls to be recorded in regard to the anti-scorbutic vitamin, but Bezssonoff<sup>22</sup> suggests that this vitamin too is a complex consisting of two substances, differing in their heat stabilities, one probably being derived from the other. Hoyle and Zilva<sup>23</sup> report that the concentrated anti-scorbutic fraction of lemon juice contains iron, phosphorus, and sulphur, and that these elements dialyse along with the vitamin. On the other hand, Vedder and Lawson<sup>24</sup> state that their concentrated preparations, made by extraction with alcohol, could be freed from phosphorus and sulphur without loss of activity. In an interesting quantitative study of the reducing power of the anti-scorbutic fraction of lemon juice towards phenolindophenol, Zilva<sup>25</sup> shows that if sufficient of this indicator be added to destroy the reducing property of the solution, the reduced leuco-compound of the indicator is re-oxidised in the air and is then further reduced by the solution. This alternate reduction and oxidation proceeds until the reducing power of the medium is destroyed. The reducing property of decitrated juice or of its active fractions is lost, like the anti-scorbutic activity, in an alkaline medium in the presence of air, but on fractionation of the juice the substance responsible is found in as high quantities in the inactive as in the active fractions. On adding the indicator to decitrated lemon juice until the former is no longer reduced, and on testing the solution so treated immediately, no very appreciable loss in the anti-scorbutic activity is observed. Neither the reducing capacity nor the anti-scorbutic activity undergoes any appreciable diminution when the decitrated juice is kept for one hour in neutral or acid solution in an autoclave at a pressure of one atmosphere. On storing, both properties deteriorate very much more quickly than in untreated decitrated juice. Zilva suggests that the stability of vitamin-C possibly depends on a sequence of reactions which are normally kept in equilibrium in the living cell—a hypothesis of great interest in

<sup>21</sup> *Proc. K. Acad. Wetensch. Amsterdam*, 1927, **30**, 376; **A.**, 1224.

<sup>22</sup> *Compt. rend.*, 1926, **183**, 1309; **A.**, 1927, 283.

<sup>23</sup> *Biochem. J.*, 1927, **21**, 1121; **A.**, 1224.

<sup>24</sup> *J. Biol. Chem.*, 1927, **73**, 215; **A.**, 702.

<sup>25</sup> *Biochem. J.*, 1927, **21**, 689; **A.**, 702.



view of the suggestion of Bezssonoff, already referred to, regarding the complex nature of this vitamin.

*Vitamin-D.*—In order to present a more complete survey of the present position of the numerous investigations in progress with regard to the formation and properties of vitamin-*D*, it will be advisable to include in the present Report some reference to matters mentioned in the Report of last year. Early in 1927 there appeared the detailed results of Heilbron, Kamm, and Morton,<sup>26</sup> who were able to show in a spectrographic study of cholesterol, before and after irradiation with ultra-violet light, that purified cholesterol contains in small amount another substance which can be accumulated in the least soluble fraction on crystallisation from ethyl acetate, that this substance possesses absorption bands in the ultra-violet at 293  $\mu$ , 280  $\mu$ , and 269  $\mu$ , whereas cholesterol itself has only general absorption, and that these bands disappear on irradiation with a concomitant appearance of anti-rachitic potency. It was suggested that this unknown substance and not cholesterol itself was closely related to the precursor of vitamin-*D*. While this work was in progress Rosenheim and Webster<sup>27</sup> in this country and Windaus and Hess<sup>28</sup> in Germany were making a detailed examination of the effects of irradiating a large number of cholesterol derivatives and related compounds. In the course of this work it was shown that the trebly unsaturated and highly labile ergosterol,  $C_{27}H_{42}O$ , gave rise to a highly potent anti-rachitic substance. It was further shown that cholesterol and the phytosterols, stigmasterol,  $C_{30}H_{48}O$ , and sitosterol,  $C_{27}H_{46}O$ , when brominated, and subsequently reduced by the action of sodium amalgam and acetic acid in order to regenerate the original sterol, were quite unable, after irradiation, to prevent the development of rickets in rats. It was suggested that the labile provitamin had been destroyed in the course of this treatment. In view of the high sensitivity of ergosterol to oxidative processes, of its ultra-violet absorption spectrum, similar to, but more intense than, that of impure "activatable" cholesterol, and of the very high degree of anti-rachitic potency developed by ergosterol on irradiation (Rosenheim and Webster state that the curative dose for rickets, developed in rats, is of the order of 1/10,000 to 1/20,000 mg. *per diem*), both Rosenheim and Webster and Windaus suggest that provitamin-*D* is ergosterol or some closely related sterol. They suggest that it is the presence of small amounts of the latter, in the proportion of about 1 part in 2000, in all specimens of cholesterol prepared from

<sup>26</sup> *Biochem. J.*, 1927, **21**, 78; **A.**, 381.

<sup>27</sup> *Ann. Reports*, 1926, **23**, 254; *Biochem. J.*, 1927, **21**, 127, 389; **A.**, 381, 487.

<sup>28</sup> *Nachr. ges. Wiss. Göttingen*, 1927, **175**, 84.

natural sources that is responsible for the development of anti-rachitic properties. Irradiated ergosterol is certainly the most potent anti-rachitic substance known and it is estimated that about 5 mg. are equivalent to about 1 litre of a good cod-liver oil. Dr. Katharine Coward is reported by Rosenheim and Webster to have detected the calcifying effect of 1/100,000 mg. of irradiated ergosterol by means of the "line" test.

Rosenheim and Webster<sup>29</sup> have published a further study of the mechanism underlying the conversion of ergosterol into vitamin-*D*, in the course of which it is shown that the maximum activity is attained within 30 minutes after exposure to the radiations of a mercury vapour lamp, the usual precautions being adopted to exclude oxidative changes. Thereafter the activity does not increase *pari passu* with the disappearance of ergosterol, but remains constant up to 4 hours' irradiation. It is suggested that after a short initial period the formation and destruction of the vitamin proceed at the same rate until the available supply of ergosterol is exhausted. It would in any case appear that the conversion of ergosterol into vitamin-*D* is not a simple unimolecular reaction. Rosenheim and Webster record the further important observation that the comparatively long-wave radiations of solar ultra-violet light are capable of activating ergosterol. The high content of cholesterol present in human skin (13 to 24%), and the presence in this cholesterol of some substance possessing the same ultra-violet absorption as ergosterol, being borne in mind, this observation is of the greatest interest in relation to the curative effect of sunlight in rickets.

In view of the results just described, it would seem that there is no serious obstacle to the belief that provitamin-*D* is identical with ergosterol. Nevertheless, the observations of Jendrassik and Keményffi<sup>30</sup> lead these authors to suggest an alternative theory. In the first place, they confirm the statements of Rosenheim and Webster and of Windaus and Hess that irradiated ergosterol provides a highly potent anti-rachitic preparation, but they have failed to confirm the observation that cholesterol, after bromination and subsequent reduction, cannot be activated by irradiation. It is also asserted that in a series of fractionation experiments inactive cholesterol, after removal of the active fraction by recrystallisation and washing, can be reactivated repeatedly. The period of irradiation used by these investigators is 1 hour and the cholesterol is irradiated in thin layers containing 0.01 g. per square cm., and it is apparently assumed that complete conversion of the provitamin into the vitamin occurs under these conditions. The successive

<sup>29</sup> *Lancet*, 1927, ii, 622; **A.**, 1224.

<sup>30</sup> *Biochem. Z.*, 1927, **189**, 180; **A.**, 1224.

development of anti-rachitic potency in inactive fractions, from which the active substance developed in previous irradiations has been removed, and especially their success in activating cholesterol after bromination, lead Jendrassik and Keményffi to the remarkable conclusion that, although cholesterol itself is not the provitamin, it gives rise to the latter in the presence of water. They also state that on withdrawal of the last traces of water from cholesterol the provitamin is destroyed and the possibility of its re-formation is lost together with a concomitant disappearance of the characteristic absorption bands, unless it be again treated with water. These remarkable suggestions of Jendrassik and Keményffi merit attention, and it appears to the Reporter that, apart from the bromination experiments, they are not incompatible with the results of Rosenheim and Webster and of Windaus. It is therefore highly desirable that the question of the activatable nature or otherwise of brominated and reduced cholesterol should be subjected to rigorous tests under widely varying conditions. It is to be noted that Jendrassik and Keményffi subjected the cholesterol which they regenerated from the dibromo-compound to two evaporations on the steam-bath with wet alcohol. Hess and Anderson,<sup>31</sup> who have separated sitosterol from corn oil into  $\alpha$ -,  $\beta$ -, and  $\gamma$ -fractions, the first-mentioned being the most soluble and least stable of the three, confirm the fact that neither the  $\beta$ - nor the  $\gamma$ -fraction could be activated by irradiation after purification by means of the respective bromo-compounds. The freshly prepared  $\alpha$ -sitosterol could be activated (omitting the bromine treatment), but Hess and Anderson are not certain of the degree of purity of their preparation.

In view of the results described above, it is obvious that the numerous observations published during the past year on the activation and fractionation of cholesterol and of its derivatives must be re-examined, but at the same time much valuable information has been accumulated which will no doubt be more readily interpreted when the chemical natures of vitamin-*D* and its precursor have been elucidated, an achievement which cannot now be long delayed.

*Vitamin-E.*—Little has been added to our information concerning the anti-sterility vitamin. Sure<sup>32</sup> and Hartwell<sup>33</sup> both report that fertility of rats is diminished, or complete sterility may be produced, by diets in which cod-liver oil is the sole source of fat and fat-soluble vitamins. Sure was able to restore fertility by supplementing the diet with 0.035% of the unsaponifiable matter from

<sup>31</sup> *J. Biol. Chem.*, 1927, **74**, 651; **A.**, 1224.

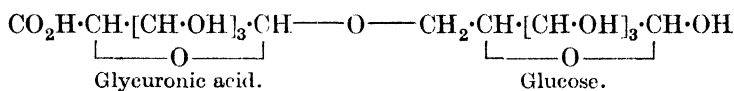
<sup>32</sup> *Ibid.*, pp. 37, 45, 71; **A.**, 905.

<sup>33</sup> *Biochem. J.*, 1927, **21**, 1076; **A.**, 1107.

cotton-seed oil, or by a large addition (10%) of butter. Hartwell confirms the advantage of butter over cod-liver oil. Simmonds, Becker, and McCollum<sup>34</sup> state that the death of rat-fœtuses through lack of vitamin-*E* is due to a crisis in their assimilation of iron, the administration of ferric citrate or wheat oil being beneficial. They report that liver oils are rich in vitamin-*E*, a result which seems to be at variance with the results of other workers on cod-liver oil.

*Specific Carbohydrates from Bacteria.*

Professor Drummond dealt in the Report for last year with the highly interesting advance in the chemistry of specific immunological reactions rendered possible by the work of Heidelberger, Avery, and their associates.<sup>35</sup> Further progress in the study of the nature of the specific polysaccharides isolated by them has been made in the past year. Heidelberger and Goebel<sup>36</sup> have shown that the polysaccharide of Type III *pneumococcus*, on acid hydrolysis, yields glucose and an acid of the type of glycuronic acid having the formula  $C_{12}H_{20}O_{12}$ . It has one half of the reducing power of glucose, gives a positive reaction with naphtharesorcinol, contains an aldehyde group, and on oxidation with nitric acid gives saccharic acid. On oxidation with barium hypoiodite<sup>37</sup> the original acid gives a dicarboxylic acid,  $C_{10}H_{18}O_9(CO_2H)_2$ , which still responds to the naphtharesorcinol reaction and yields the same amount of furfuraldehyde as the original acid. It is therefore deduced that the latter is an aldobionic acid composed of one molecule of glucose and one of glycuronic acid combined in glucosidic linking through the aldehyde group of the latter. The following formula is therefore to be ascribed to this substance :



The reducing group of the glycuronic acid residue may be attached to the glucose residue in the position 6 shown, or to any one of the positions 2, 3, and 4. The evidence does not yet permit of a choice being made between these possibilities.

Goebel<sup>38</sup> has obtained from the specific polysaccharide of Friedländer's type *A* bacillus an aldobionic acid which is composed likewise of glycuronic acid and glucose apparently linked in the same way as the components of the *pneumococcus* acid, with which it is isomeric. One would suggest that the presence of one of the

<sup>34</sup> *J. Amer. Med. Assoc.*, 1927, **88**, 1047; **A.**, 1224.

<sup>35</sup> *Ann. Reports*, 1926, **23**, 248.

<sup>36</sup> *J. Biol. Chem.*, 1927, **70**, 613; **A.**, 77.

<sup>37</sup> *Ibid.*, **74**, 613; **A.**, 1114.      <sup>38</sup> *Ibid.*, p. 619; **A.**, 1114.

possible linkings just mentioned, other than that present in the *pneumococcus* acid, is responsible for this isomerism.

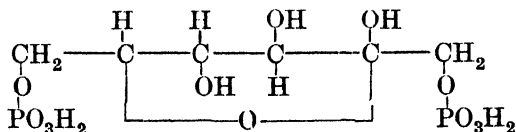
The parent polysaccharides from which these interesting sugar acids are derived are regarded as being composed of units of the aldobionic acid in the case of the *pneumococcus* substance, and of units composed of two molecules of the aldobionic acid and one molecule of glucose in the case of the Friedländer substance.

To the list of organisms which yield specific carbohydrates with immunological properties is to be added the cholera vibrio.<sup>39</sup>

### *Organic Phosphates and Lactacidogen.*

During the past year much attention has been directed to the chemistry of the known hexosephosphates and to the question of the presence and functions of organic phosphates in muscle tissue. The most noteworthy advances have been made in the chemistry of the first discovered hexosephosphate, the diphosphate of yeast fermentation, in the chemistry of lactacidogen, the hexosephosphate of muscle, and in the demonstration that there are present in muscle certain organic nitrogenous phosphates which appear to play a highly important rôle in muscle function.

*The Hexosediphosphoric Acid of Yeast Fermentation.*—Morgan<sup>40</sup> has been able to prepare from this acid the  $\alpha$ - and  $\beta$ -methylhexoside-diphosphoric acids by subjecting the parent substance to the Fischer-Speyer acid-methyl alcohol process. The two stereoisomerides were obtained in the form of their brucine and barium salts. The glucosidic methyl group of the  $\alpha$ -acid is more readily removed by hydrolysis than that of the  $\beta$ -acid, but neither hexoside is hydrolysed by emulsin. On the other hand, invertase causes a partial removal of the methyl group of the  $\alpha$ -acid, but it does not affect the  $\beta$ -acid. Of great interest is the observation that the bone enzyme (phosphatase) rapidly removes the phosphoric acid groups of the  $\beta$ -acid, leaving a strongly laevorotatory, non-reducing substance possessing the properties of a methylfructoside. An extension of these results recently described by Morgan and Robison<sup>41</sup> has led to the suggestion that the structure of hexosediphosphoric acid is that of  $\gamma$ -fructose-1 : 6-diphosphoric acid :



<sup>39</sup> Landsteiner and Levine, *J. Exp. Med.*, 1927, **46**, 213.

<sup>40</sup> *Biochem. J.*, 1927, **21**, 675; **A.**, 749.

<sup>41</sup> Report of the Meeting of the Biochemical Society (Dec. 9th), *J. Soc. Chem. Ind.*, 1927, **46**, 1183.

By the action of bone phosphatase on the  $\alpha$ - and  $\beta$ -methylhexosidediphosphoric acids, the corresponding  $\alpha$ - and  $\beta$ -methylhexosides were obtained, and these underwent rapid hydrolysis at room temperature on being treated with 0.01*N*-hydrochloric acid to yield a laevorotatory sugar corresponding to  $\alpha$ -fructose. Such behaviour at once suggests one of the "reactive" butylene-oxidic types of sugar and this was confirmed by converting the  $\beta$ -methylhexoside by methylation into the corresponding tetramethyl  $\beta$ -methylhexoside. The latter had  $[\alpha]_{\text{D}}^{20} - 6.8^\circ$ , and on hydrolysis yielded an  $\alpha\beta$ -tetramethyl hexose having  $[\alpha]_{\text{D}}^{20} + 30^\circ$  in close agreement with the known rotation of  $\alpha\beta$ -tetramethyl  $\gamma$ -fructose, and widely divergent from that of the corresponding normal (amyleno-oxidic)  $\alpha\beta$ -tetramethyl fructose, which has  $[\alpha]_{\text{D}} - 142^\circ$ . Morgan and Robison seem justified in inferring that the existence of the unstable butylene-oxidic ring in conjunction with an unsubstituted reducing group makes it very probable that the second phosphoric acid group occupies position 6, although it is obvious that the proof is not absolute. This result should not be regarded as unexpected in view of the known fact that all hitherto described naturally occurring compounds of fructose have been shown to exist in the  $\gamma$ - or butylene-oxidic form, so that hexosediphosphoric acid would appear to fall into line with other fructose compounds. Schlubach and Rauchenberger<sup>42</sup> have recorded the complete methylation of hexosediphosphoric acid *via* the silver salt, which on treatment with methyl iodide yielded tetramethyl hexosediphosphate, and on further treatment with silver oxide and methyl iodide afforded tetramethyl trimethylhexosediphosphate, which is reported to have  $[\alpha]_{\text{D}} + 20.77^\circ$  in chloroform solution. It would be of great interest to know if the latter were susceptible to the action of any phosphatase preparation.

*The Hexosemonophosphoric Acid of Yeast Fermentation.*—Neuberg and Leibowitz<sup>43</sup> have made a study of the hexosemonophosphoric acid first isolated from yeast fermentations by Robison. They arrive at the conclusion that the discrepancies between the reducing power after hydrolysis of the ester with taka-diastrase, as determined by copper (Bertrand) and by hypiodite (Willstätter-Schudel) methods, cannot be explained, in view of the polarimetric findings, by assuming the presence of a mixture of 85% of glucose with 15% of fructose. The hexosemonophosphoric acid is thought to consist of from 80 to 90% of a homogeneous substance which suffers secondary changes in the sugar residue on being hydrolysed. Meyerhof and Lohmann,<sup>44</sup> also employing the method of Willstätter and Schudel,

<sup>42</sup> *Ber.*, 1927, **80**, 1178; **A.**, 644.

<sup>43</sup> *Biochem. Z.*, 1927, **184**, 489; **A.**, 700. <sup>44</sup> *Ibid.*, 1927, **185**, 13; **A.**, 697.

conclude that Robison's monophosphate has a higher aldose value than Neuberg's, a result which is not surprising in view of Morgan and Robison's investigations of the yeast diphosphoric acid from which Neuberg's acid is derived. In a further publication, Neuberg and Leibowitz<sup>45</sup> record the conversion of hexosediphosphoric acid of yeast into Neuberg's monophosphate by the action of taka-diastase, and of Robison's monophosphate into the diphosphate by the action of bottom yeasts. This is the first record of the preparation of the Neuberg monophosphate by strictly biological methods, and the conversion of Robison's monophosphate into the typical yeast diphosphate probably involves, according to our present conception of the relationship of these two compounds, the preliminary removal of the phosphoric acid group. Euler and Myrbäck<sup>46</sup> also state that when Robison's hexosemonophosphate is treated with dried bottom yeast, one half is fermented and the other half is converted into the diphosphate.

An interesting point in the biochemistry of the carbohydrates, involving the behaviour of sugar phosphates, has been raised by Professor Robinson.<sup>47</sup> He points out that in the hydrolysis of phosphoric esters there is much evidence to suggest that, if the oxygen atom be directly attached to an asymmetric carbon atom, optical inversion should in many cases be observed. It has always been difficult to explain the formation of glucose from galactose, or the reverse change, without assuming a profound disruption of the carbohydrate molecule. Professor Robinson now suggests that the galactose configuration may be derived from that of a glucose-4-phosphoric acid by a dephosphorylation involving a Walden inversion. This hypothesis is highly suggestive in view of the widespread occurrence of sugar phosphates in nature. It is to be noted that it would be excluded if glucose possessed a butylene-oxidic structure. Levene<sup>48</sup> has criticised this hypothesis unfavourably in pointing out that the acid hydrolysis of glucose-3-phosphoric acid is not accompanied by any optical inversion, but the original theory presumably did not regard every or any method of hydrolysis as necessarily involving the inversion. Professor Robinson has also suggested that the pentose of plant nucleic acid, which is isolated in the form of the rare sugar *D*-ribose, may *in situ* be the much commoner *D*-xylose, the removal of the phosphoric acid group from the latter during hydrolysis inverting the configuration of (necessarily) the 3-carbon atom. This view also is criticised by Levene.

<sup>45</sup> *Biochem. Z.*, 1927, **187**, 481; **A.**, 993.

<sup>46</sup> *Z. physiol. Chem.*, 1927, **167**, 236; **A.**, 794.

<sup>47</sup> *Nature*, 1927, **120**, 44; **A.**, 960.

<sup>48</sup> *Ibid.*, 1927, **120**, 621; **A.**, 1225.

*Lactacidogen*.—During the period covered by this Report the chemistry of lactacidogen has undergone a modification which will probably re-orient many investigations of the chemical mechanisms underlying muscle contraction. Embden and Zimmermann<sup>49</sup> in 1924 identified muscle lactacidogen with the hexosediphosphoric acid of yeast fermentation, since the two substances were shown to form the same neutral brucine salt. The method of isolation of lactacidogen which these investigators used at that time involved the treatment of the muscle press-juice with glycogen, sodium fluoride, and sodium bicarbonate, with the view of removing, by a process of fermentative re-synthesis, the free phosphate present in the press-juice. It was thought that this synthetic process involved merely the re-formation of lactacidogen which had suffered degradation during the extractive manipulations. That this procedure yields a hexosediphosphoric acid identical with that produced during yeast fermentation has recently been confirmed by Pryde and Waters,<sup>50</sup> who obtained a brucine hexosediphosphate from rabbit's muscle with a specific rotation,  $[\alpha]_{5461}^{18} - 30.7^\circ$ , identical with that of a carefully purified preparation of the brucine salt of the yeast acid. During the past year Embden and Zimmermann<sup>51</sup> have isolated lactacidogen from rabbit's muscle by a modified process which omits the fermentative re-synthesis using glycogen and fluoride, and they have obtained, instead of hexosediphosphoric acid, a hexosemonophosphoric acid—an observation which has also been confirmed by Pryde and Waters.<sup>52</sup> Embden and Zimmermann state that the new monophosphate differs from the two previously known natural monophosphates (Robison's and Neuberg's), but Pryde and Waters have encountered anomalies in the rotation and solubility of their various preparations which lead them to suspect the homogeneity of the monophosphate obtained by them. Embden and Zimmermann have shown that the new muscle monophosphate is converted by muscle press-juice into lactic acid, and by muscle press-juice, glycogen, and fluoride, into hexosediphosphoric acid. They are therefore disposed to identify lactacidogen with the new monophosphate. In the absence of the artificial re-synthesising solutions, neither Embden and Zimmermann nor Pryde and Waters were able to detect the presence of any diphosphoric acid. It is none the less possible that the temporary formation of the diphosphate may play some part in the muscle process (compare p. 261).

<sup>49</sup> *Ann. Reports*, 1925, 22, 224.

<sup>50</sup> Report of the Meeting of the Biochemical Society (Dec. 9th), *J. Soc. Chem. Ind.*, 1927, 46, 1182.

<sup>51</sup> *Z. physiol. Chem.*, 1927, 167, 114; A., 749.

<sup>52</sup> *Loc. cit.*



*Adenylic Acid.*—In the course of the extraction of the monophosphoric acid from rabbit's muscle, Embden and Zimmermann<sup>53</sup> encountered a nitrogenous organic phosphate which they were able to identify as adenylic acid—an observation which again has been confirmed by Pryde and Waters.<sup>54</sup> It would appear highly probable that adenylic acid is the parent substance of inosinic acid, long known to be a constituent of muscle extractives, since a simple process of deamination of the former would yield the latter. That such a process, involving release of nitrogen, may play some part in the contractile mechanism is suggested by a growing body of evidence, which will be considered shortly. Meanwhile mention must be made of another nitrogenous organic phosphate for which a place will probably have to be provided in muscle chemistry.

*Phosphagen.*—Eggleton and Eggleton,<sup>55</sup> in determining the inorganic phosphate of muscle, found that methods such as those of Briggs or Embden, in which acid reagents are used, gave results, on the resting gastrocnemius of the frog, which were higher, by some 70 mg. P per 100 g. of muscle, than the results obtained by a method such as the Bell-Doisy, which is carried out in a mildly alkaline solution and gave results of the order 20 to 25 mg. P per 100 g. of tissue. They found that the discrepancy was due to the presence in the muscle of a labile organic phosphate which was rapidly broken down in acid solution to form inorganic phosphate. In a further study<sup>56</sup> it was shown that this labile organic phosphate participates in the chemical mechanism of contraction and is completely broken down when the muscle is fatigued in tetanus. No restitution of the organic phosphate was observed under anaërobic conditions, but in the presence of oxygen it is rapidly re-formed and an equivalent amount of inorganic phosphate is lost. This aërobic restitution process is apparently more rapid than the removal of lactic acid which occurs during the recovery phase. Eggleton and Eggleton suggested the name "phosphagen" for this unknown labile phosphoric acid compound. Fiske and Subbarow<sup>57</sup> in America encountered the same labile phosphorus compound and showed that in the normal resting voluntary muscle of the cat, what had previously been regarded as "inorganic phosphate" consisted of some 60 to 75 mg. of labile organic phosphate and some 20 to 25 mg. of true inorganic phosphate per 100 g. of tissue, figures which are remarkably close to those of Eggleton and Eggleton for the frog. Fiske and Subbarow also made the highly interesting

<sup>53</sup> *Z. physiol. Chem.*, 1927, **167**, 137; **A.**, 787.

<sup>54</sup> *Loc. cit.*

<sup>55</sup> *Biochem. J.*, 1927, **21**, 190; **A.**, 271.

<sup>56</sup> Eggleton and Eggleton, *J. Physiol.*, 1927, **63**, 155; **A.**, 990.

<sup>57</sup> *Science*, 1927, **65**, 401; **A.**, 990.

observation that the labile phosphorus compound was composed of creatine and phosphoric acid, an observation which was shortly afterwards confirmed by Eggleton and Eggleton,<sup>58</sup> one molecule of creatine being associated with each atom of phosphorus.

These observations are obviously of the greatest importance in relation to all previous determinations of the inorganic phosphoric acid of muscle, and a further point of interest emerges when it is seen that incubation of a chopped muscle in the presence of sodium fluoride leads to the conversion of "phosphagen" into an acid-stable organic phosphate. It would appear possible that "phosphagen" is the source of the second phosphoric acid residue which is added on to Embden and Zimmermann's muscle hexosemonophosphate when the latter is treated with muscle press-juice, glycogen, and fluoride. The part played by "phosphagen" in the contractile process is not yet clear. That most, or probably all, of the muscle creatine is present in the resting muscle in combination with phosphoric acid is strongly suggested by the fact that creatine, like "phosphagen," is most abundant in voluntary muscle, less so in cardiac muscle, and present only in traces in involuntary muscle.

#### *Ammonia Formation in Muscle.*

In the Report for last year the observations of Hoet and Marks<sup>59</sup> on the precipitate rigor, which sets in immediately after death from an overdosage of insulin or from excessive thyroid feeding, in which conditions the muscles contain no glycogen, little or no lactacidogen, and show no accumulation of lactic acid, suggested that a possible determining factor in this type of rigor was an alkaline phase. At the time little or nothing was known of any possible source of alkalinity, but since then it has been shown that the formation of ammonia is probably an integral part of the muscle process, and this suggestion gains strength in view of the occurrence in muscle of the nitrogenous compounds which we have just considered.

Parnas and Mozolowski<sup>60</sup> have shown that the maceration of vertebrate muscle in water or saline leads to the formation of about 5 mg. of ammonia per 100 g. of muscle. This formation of ammonia is inhibited by a borate buffer of  $p_H$  9.3. It is suggestive that this traumatic formation of ammonia is most marked in voluntary muscle, less so in heart and smooth muscle, and absent in glandular tissues. The process of formation is a rapid one, being complete in the case of the frog's gastrocnemius in 90 seconds. On extracting muscle with a borate solution the ammonia precursor is obtained

<sup>58</sup> *J. Soc. Chem. Ind.*, 1927, 46, 485.

<sup>59</sup> *Ann. Reports*, 1926, 23, 242.

<sup>60</sup> *Biochem. Z.*, 1927, 184, 399; *A.*, 694.

together with an enzyme which acts upon it, and ammonia formation occurs on simple neutralisation of this extract, although at a much slower rate than in the intact cellular tissue. The precursor is stable in both acid and alkaline solutions. Since the ammonia of the intact muscle is increased by electrical stimulation and by strychnine convulsions, it is inferred that its release is definitely related to contraction. Habs,<sup>61</sup> in association with Embden, also has studied the occurrence of ammonia in muscle, and shows that its formation in muscle pulp runs parallel with the liberation of free phosphate. It is an attractive hypothesis to regard adenylic acid as the precursor of the muscle ammonia, and Embden<sup>62</sup> has indeed advanced this suggestion, but Parnas points out that there would be required for the traumatic formation of 5 mg. % of ammonia 25 mg. % of purine nitrogen as adenylic acid. Now the *total* purine nitrogen of the frog's muscle, including that of nuclear substances, is only 35 mg. %. For the muscles of other animals, too, almost the whole of the purine nitrogen would have to be present in the form of adenylic acid should this substance be the sole precursor of the ammonia determined by Parnas and Mozolowski. It is difficult to see how creatine can be regarded as the ammonia precursor, nor is there any evidence to suggest that it is. As Habs points out, adenylic acid is the only substance capable of forming ammonia so far detected in the muscle and as such it merits further consideration. In a comparison of the chemical processes of "trained" (subjected to short, periodic, daily faradisation in the intact animal) as compared with "untrained" muscle, Embden and Habs<sup>63</sup> show that the "trained" muscle shows a marked increase in glycogen content and a small but definite increase in the residual nitrogen. They do not suggest what particular nitrogen compound or compounds are increased, but do show that the creatine figures are not affected.

It is obviously difficult at the moment to correlate this newer work on the chemistry of muscle with the older work on lactic acid formation, but it seems certain that a considerable widening of our views on the whole subject must soon result.

#### *Lactic Acid-forming Enzymes from Muscle.*

Much interesting work has been published on the processes of lactic acid formation in muscle, but in the opinion of the Reporter the most significant advance is the isolation by Meyerhof of an active lactic acid-forming enzyme from muscle. This was referred to in the Report of last year,<sup>64</sup> but since that date Meyerhof has

<sup>61</sup> *Z. physiol. Chem.*, 1927, 171, 40.

<sup>62</sup> *Klin. Wochenschr.*, 1927, 6, 628.

<sup>63</sup> *Z. physiol. Chem.*, 1927, 171, 16.

<sup>64</sup> *Ann. Reports*, 1926, 23, 242.

himself provided a useful summary,<sup>65</sup> and many more recent results have been published which justify a detailed account in the present year's Report.

Meyerhof<sup>66</sup> has shown that it is possible to separate completely the lactic acid ferment from frog or rabbit muscle and to obtain it in aqueous solution free from the carbohydrates of the muscle. Following a method of Buchner, it is possible, by precipitation with acetone, to obtain a dry enzyme preparation which, when redissolved, possesses 40% of the activity of the original extract. For example, when glycogen is added to it, the enzyme preparation shows for several hours an activity about as great as that of the minced muscle at the same temperature, when calculated against muscle weight. Calculated against the dry weight of the extract, its activity is at least five times as great as that of the muscle pulp. A co-enzyme, which is dialysable and thermostable, can be separated from the enzyme mixture. It has been shown that this water-soluble lactic acid ferment splits hexoses only under special conditions, which will be referred to later, but on the other hand, in the presence of inorganic phosphate<sup>67</sup> it readily acts upon starch, glycogen, the starch components amylose and amylopectin, and the simpler compounds derived from them, such as tri- and di-hexosans, splitting them all to lactic acid with about the same velocity. During hydrolysis of the polysaccharides, a phosphoric ester accumulates at first quickly, then more slowly, and this ester can be completely decomposed into lactic acid and phosphate by warming at 37°. The muscle enzyme also acts, but rather more slowly, upon the hexosediphosphoric acid of yeast. It would, however, appear that different enzymes are concerned in these reactions. For instance, it is easy to separate from the enzyme complex the enzyme which attacks hexosediphosphoric acid. Heating at 37° for 15 minutes destroys the capacity of the extract to split glycogen and other polysaccharides, but scarcely affects its capacity to split the hexosediphosphoric acid to lactic acid. Removal of the co-ferment by dialysis also yields an enzyme solution which still splits hexosediphosphoric acid, but which is without action on glycogen or starch. This varying behaviour towards glycogen and hexosediphosphoric acid depends upon the fact that brief heating at 37°, or removal of the co-ferment, destroys the ability of the enzyme extract to esterify the cleavage products of the polysaccharide with inorganic phosphate. Thus the labile hexose first formed by the cleavage of the glycogen must first be esterified with

<sup>65</sup> *J. Gen. Physiol.*, 1927, **8**, 531.

<sup>66</sup> *Biochem. Z.*, 1926, **178**, 395, 462; *A.*, 1927, 75.

<sup>67</sup> Meyer, *ibid.*, 1927, **183**, 216; *A.*, 590.

phosphoric acid before splitting and lactic acid formation can occur. This is well illustrated by the delayed appearance of lactic acid when the muscle enzyme preparation acts upon glycogen or starch, as compared with its immediate appearance when the substrate is hexosediphosphoric acid.

Meyerhof's muscle enzyme, even in the presence of the co-enzyme, acts but slowly on the fermentable hexoses,<sup>68</sup> but by extracting baker's yeast with water and precipitating the extract with alcohol, there is obtained a substance which, when added to the muscle extract, greatly accelerates the rate of formation of lactic acid from hexoses. In neutral solution at 0°, this activator can be preserved indefinitely, but it is readily destroyed by heat and by acids and alkalis. Treatment of a hexose with muscle extract in the presence of the activator leads to a rapid formation of lactic acid and a parallel disappearance of inorganic phosphate. At the point when all the inorganic phosphate has been used up, the velocity of formation of lactic acid falls rapidly and subsequently runs parallel to the liberation of inorganic phosphate, that is to say, in the second stage lactic acid and phosphate are being formed in equimolar proportion. If at the end of the first stage a further addition of inorganic phosphate be made, the original velocity of lactic acid formation is restored.

Meyerhof and Lohmann<sup>69</sup> have investigated the action of the muscle extract on the hexosemonophosphates obtained from natural sources, and upon certain synthetic hexosemonophosphates. It is an interesting fact that the muscle extract is almost without action on the synthetic monophosphates, whereas the natural monophosphates undergo a transformation similar to that of the polysaccharides, hexosediphosphoric acid, and the fermentable hexoses, there being a rapid formation of lactic acid and a disappearance of inorganic phosphate, followed by a slower production of lactic acid running parallel with the reappearance of inorganic phosphate. In the case of the monophosphates, as with the polysaccharides, the presence in the muscle extract of the co-ferment is necessary.

Meyerhof and Meyer<sup>70</sup> have described a method of purifying the lactic acid enzyme of muscle and a final preparation is obtained, after adsorption on aluminium hydroxide made according to Willstätter's method, which is capable of forming 1.0 to 1.5 mg. of lactic acid in each hour per mg. of protein present in the purified enzyme extract. Since in this process of purification the co-enzyme is removed, boiled muscle juice must be added before any action on polysaccharides and

<sup>68</sup> *Biochem. Z.*, 1927, **183**, 176; **A.**, 590.

<sup>69</sup> *Ibid.*, **185**, 113; **A.**, 697.

<sup>70</sup> *J. Physiol.*, 1927, **64**, XVI; **A.**, 1112.

hexosemonophosphates is observed. Meyerhof and Meyer also state that in addition to enzyme and co-enzyme a hydrolysable ester is necessary and that the latter can be recovered from the baryta precipitate of fresh muscle extract or boiled juice. This substance is not Embden's lactacidogen (monophosphate), but is stated to be an ester which behaves as a diphosphoric ester. Its rôle would therefore appear to correspond to that of hexosediphosphoric acid in inducing alcoholic fermentation in yeast juice.

These results, which have been described in some detail in view of their importance, show many striking similarities to the processes of yeast fermentation and would appear strongly to suggest that both hexosemonophosphates and hexosediphosphates are intermediate stages in the enzymic degradation of carbohydrate both by muscle extract and by yeast. In regard to this question it is interesting to note that Harden and Henley<sup>71</sup> have re-examined the data upon which the equation of alcoholic fermentation was originally based. They now find that the ratio  $\text{CO}_2/\text{total P esterified}$  is on the average 0.9, indicating that about 10% of the phosphorus is esterified without equivalent evolution of carbon dioxide. They suggest that the product of this esterification is probably a monophosphate. The ratio  $\text{CO}_2/\text{diphosphate}$  is on the average 2.38, but varies considerably in individual cases. The fact that it is always somewhat greater than 2, as required by the original equation of Harden and Young, suggests that the diphosphate is originally produced in accordance with the equation, but that a portion of this is subsequently hydrolysed with the formation of a monophosphate.

#### *Insulin and its Rôle in Carbohydrate Metabolism.*

*Crystalline Insulin.*—In the Report of last year mention was made of the claims of Funk and of Abel regarding the isolation of insulin in a pure state.<sup>72</sup> During the past year both these workers have made further publications of great interest. Abel and his associates<sup>73</sup> state that when pyridine is added to an acid solution of insulin, containing brucine acetate in amount sufficient to bring the  $p_H$  to 5.55–5.65, the insulin separates in a crystalline condition. On applying this method to the purification of commercial insulin there was obtained, by working up the pyridine precipitate and the mother-liquors, 0.4848 g. of crystalline insulin from 2.001 g. of the commercial insulin powder. Abel has naturally considered the possibility that the crystals obtained are not really insulin but those of an inactive compound containing a very small quantity of highly

<sup>71</sup> *Biochem. J.*, 1927, **21**, 1216; **A.**, 1113.

<sup>72</sup> *Ann. Reports*, 1926, **23**, 238.

<sup>73</sup> Abel, Geiling, Rouiller, Bell, and Wintersteiner, *J. Pharm. Exp. Ther.*, 1927, **31**, 65; **A.**, 701.

active material adsorbed on their surfaces. This possibility is dismissed on what appears to be convincing evidence. Crystalline insulin has an activity exceeding 40 international units per mg., and it gives the biuret, Pauly, Millon, and ninhydrin reactions. Tryptophan is said to be absent. The simplest formula corresponding to the analyses is  $C_{45}H_{69}O_{14}N_{11}S \cdot 3H_2O$ , which should be compared with the earlier alternative suggestions of Funk,  $C_{69}H_{102}O_{22}N_{18}S$  and  $C_{74}H_{114}O_{24}N_{20}S$ . Crystallographic observations suggest that insulin is dimorphous. This observation is of interest in view of Funk's most recent claims.<sup>74</sup> Funk states that insulin may be fractionated to yield insulin-*A* and insulin-*B*. The former, which is present in larger proportion, decreases the blood sugar of normal rabbits and of those having high initial blood sugars. On the other hand insulin-*B* is said to increase the blood sugar and to cause dilution of the blood with large retention of water. Du Vigneaud<sup>75</sup> has recently published observations which corroborate in large measure the statements of Abel. For example, he has been able to obtain a highly active crystalline preparation of insulin by following the method of Abel. Du Vigneaud's preparation contains labile sulphur which he states is present in a disulphide form. He regards insulin as most probably a derivative of cystine and points out that the behaviour of the sulphur in insulin is quite parallel to that of the sulphur in amino-acid derivatives of cystine. It is suggested, in view of the probable presence of a disulphide grouping, that Abel's formula should be doubled. On the basis of these results, it now appears highly probable that sulphur is an integral part of the insulin molecule, a suggestion first made by Dudley<sup>76</sup> in 1923, when he formed the impression that insulin was a complex protein derivative.

*The Rôle of Insulin.*—Thannhauser and Jenke<sup>77</sup> recently reported that glucosone, the keto-aldehyde derivative common to glucose, mannose, and fructose, was utilised by diabetics. Hynd<sup>78</sup> now reports that, unlike dihydroxyacetone, which is also utilised by diabetics (but compare p. 263) and readily alleviates the hypoglycæmic symptoms, glucosone produces no alleviation. On the contrary, when it is injected into mice a condition is produced similar to that following insulin injection, resulting in convulsions, coma, and death. Lactosone and maltosone, the corresponding keto-aldehydes derived from lactose and maltose, are quite negative in

<sup>74</sup> *Science*, 1927, **65**, 39; **A.**, 594.

<sup>75</sup> *J. Biol. Chem.*, 1927, **75**, 393.

<sup>76</sup> *Ann. Reports*, 1923, **20**, 178.

<sup>77</sup> *Arch. exp. Path. Pharm.*, 1926, **110**, 500; **A.**, 1926, 317.

<sup>78</sup> *Proc. Roy. Soc.*, 1927, **B**, **101**, 244; **A.**, 480.

their actions. The glucosone effect, like that produced by insulin, is slightly modified by administration of glucose, and appreciably so by adrenaline and pituitrin. Despite the similarity between the actions of insulin and glucosone, the latter does not lower the blood sugar; on the other hand, increases of from 0.16 to 0.24% have been observed in mice. Hynd interprets these observations by suggesting that insulin is an oxidase which catalyses the conversion of glucose into glucosone, that glucosone is an obligate first step in the oxidation of glucose, and that therefore utilisation of glucose is diminished or lacking if insulin be deficient or absent, as it would be in the blood of pancreatic diabetics. Should the concentration of glucosone become too high, owing to excessive insulin administration, convulsions would occur just as they do when glucosone is injected directly. On this view the convulsions of insulin hypoglycæmia are not to be ascribed to the lowered blood sugar *per se*, but to the conversion into glucosone of that part of the sugar which disappears and undergoes oxidation. The glucosone symptoms are inhibited by a previous injection, and markedly relieved by a subsequent injection of acetoacetic acid. Glucosone would appear to be functioning here as a ketolytic substance in Shaffer's sense. These conclusions are in accord with the views of Thannhauser and Jenke, since these workers formed the view that the disturbance in the diabetic is due, not to inability to convert glucose after glycogenolysis into a utilisable form (*e.g.*,  $\gamma$ -glucose), but to the inability to convert glucose into glucosone, which is then utilised for the synthesis of glycogen or oxidised. It would appear that glucosone is capable of forming glycogen even more readily than is fructose. Lambie<sup>79</sup> is in essential agreement with the suggestion that the diabetic primarily lacks the power of transforming glucose into some intermediate product which can be oxidised by the diabetic as well as by the normal subject. But in view of the earlier results of Kermack, Lambie and Slater,<sup>80</sup> and of Lambie and Redhead,<sup>81</sup> he attaches great importance to dihydroxyacetone as the intermediate product. Markowitz and Campbell<sup>82</sup> have, however, arrived at diametrically opposite views regarding the utilisability of dihydroxyacetone by the diabetic, stating that, when it is administered to depancreatized dogs, its concentration in the blood steadily falls, while the concentration of glucose rises, and ultimately the dihydroxyacetone is quantitatively excreted as glucose. They therefore do not regard dihydroxyacetone as an

<sup>79</sup> *J. Soc. Chem. Ind.*, 1927, **46**, 300; **A.**, 989.

<sup>80</sup> *Biochem. J.*, 1926, **20**, 486; 1927, **21**, 40; **A.**, 1926, 861; 1927, 282.

<sup>81</sup> *Ibid.*, 1927, **21**, 549; **A.**, 693.

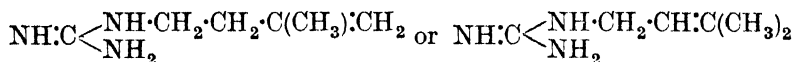
<sup>82</sup> *Amer. J. Physiol.*, 1927, **80**, 548, 561; **A.**, 693.



intermediate in the catabolism of carbohydrate. It is, in their view, not oxidised and has no anti-ketogenic action.

*Synthalin*.—Clinicians have recently devoted some attention to a synthetic preparation called "synthalin," which is a decamethylene-diguanidine derivative ( $\alpha\omega$ -diguanidyldodecane), and was introduced by Frank, Nothmann, and Wagner <sup>83</sup> as a substitute for insulin, but having the advantage over the latter in that it could be given effectively by mouth. Simola <sup>84</sup> has published a detailed examination of the physiological action of "synthalin" and finds very considerable differences between the action of the natural hormone and the artificial substitute. For example, the hypoglycæmia produced by the latter is far less marked, appears only after some hours, and is more lasting than that produced by insulin. In addition to its hypoglycæmic action, "synthalin," like insulin, depresses the blood inorganic phosphate, but in an irregular manner. If a poisonous dose be administered, the inorganic phosphate rises sharply, reaching twice its normal value after 24 hours. Lactic acid also is increased in the blood after "synthalin" administration. Toxic symptoms of guanidine poisoning often develop and it would appear from clinical experience on the human subject that the toxic nature of the artificial substitute is likely severely to restrict its use. There is, however, no doubt that it does produce some increase of sugar utilisation in the diabetic; for instance, Lublin <sup>85</sup> reports that diabetics, treated with "synthalin" by mouth, show an increase in the respiratory quotient following the administration of glucose.

During the past year two studies have been published on the action of galegine. Galegine is a guanidine derivative shown by Barger and White <sup>86</sup> to have the constitution :



Simmonet and Tanret <sup>87</sup> have shown that subcutaneous injection of galegine sulphate in rabbits produces in most cases hypoglycæmia, but in some cases the condition is preceded or replaced by hyperglycæmia. The effect is very similar to that of insulin and may be relieved somewhat by an injection of glucose. Müller and Reinwein <sup>88</sup> have published very similar findings. They state that,

<sup>83</sup> *Deut. med. Wochenschr.*, 1926, **52**, 2067.

<sup>84</sup> *Z. physiol. Chem.*, 1927, **168**, 274; **A.**, 900.

<sup>85</sup> *Arch. exp. Path. Pharm.*, 1927, **124**, 118; **A.**, 896.

<sup>86</sup> *Biochem. J.*, 1923, **17**, 827; **A.**, 1924, i, 272.

<sup>87</sup> *Compt. rend.*, 1927, **184**, 1600; *Bull. Soc. chim. biol.*, 1927, **9**, 908; **A.**, 991.

<sup>88</sup> *Arch. exp. Path. Pharm.*, 1927, **125**, 212; **A.**, 1109.

when administered to rabbits or when given in large doses to dogs, it raises the blood-sugar. When it is given in small doses to dogs, the blood-sugar is lowered, and in the case of depancreatized dogs both blood and urinary sugars are lowered. The hyperglycæmic action is antagonised by ergotamine, and when the two substances are administered together hypoglycæmic convulsions may be produced in both rabbit and dog.

*Hæmoglobin, Hæmochromogen, and Cytochrome.*

Although the subject of hæmoglobin has been dealt with by Professor Drummond in the Annual Reports for the two preceding years,<sup>89</sup> the many important advances in the study of this respiratory pigment and related substances have, until very recently, proved difficult to correlate with one another, and it is felt that a survey of the developments of the past two or three years is called for in the present Report. The Reporter is encouraged in undertaking this task in virtue of a very helpful summary of the present position published by Keilin.<sup>90</sup>

The complex substituted tetrapyrrole compounds called porphyrins form the basis of the respiratory pigments which we shall consider in the present section of this Report. A large series of porphyrins of animal and vegetable origin is known, and some, notably ætioporphyrin, have been synthesised. They form characteristic compounds with metals for which Schumm<sup>91</sup> has suggested the general name porphyratins. Hæmatin or hæm, the prosthetic group of hæmoglobin, which is an iron porphyratin, exists in two forms, oxyhæmatin and reduced hæmatin, the latter being the hæm of Anson and Mirsky.<sup>92</sup> These two hæmatins, differing in their state of oxidation, also differ in solubility, colour, absorption spectrum, and gas-combining power. Furthermore, characteristic differences are shown by the two hæmatins according as they are present in alkaline, neutral, or acid solution. The differences in the absorption spectra are slight in the case of reduced hæmatin under these varying conditions of reaction, but, on the other hand, marked differences are shown by oxyhæmatin under the same conditions. An important advance in the study of the relationship of these iron-porphyrin compounds to hæmoglobin and related pigments was rendered possible by Hill and Holden<sup>93</sup> when, in 1926, they succeeded in separating from hæmoglobin the *natural* globin with which the prosthetic group is associated, and they were able to show

<sup>89</sup> *Ann. Reports*, 1925, **22**, 237; 1926, **23**, 249.

<sup>90</sup> *Soc. Biol., Réunion Plénière*, May 1927 (Reprint).

<sup>91</sup> *Z. physiol. Chem.*, 1926, **152**, 147; *A.*, 1926, 537.

<sup>92</sup> *Ann. Reports*, 1925, **22**, 237.

<sup>93</sup> *Biochem. J.*, 1926, **20**, 1326; *A.*, 1927, 67.

that their natural globin combined with neutral oxyhæmatin, over the range  $p_H$  5 to 10, to yield methæmoglobin. Since methæmoglobin may be readily converted into reduced hæmoglobin and since the latter, shaken with air, forms oxyhæmoglobin, the natural respiratory pigment may be synthesised in this way from its components. If in place of oxyhæmatin reduced hæmatin (*i.e.*, hæm) be used, it also combines with natural globin (at  $p_H$  9.0) to yield reduced hæmoglobin directly. Hill and Holden were able to show that natural globin may also combine with porphyrins other than that of hæmoglobin, and even with porphyrins containing, not iron, but other metals such as manganese, cobalt, nickel, copper, zinc, and tin. The absorption bands of the compounds so obtained all show a displacement towards the blue end of the spectrum when compared with the bands of hæmoglobin. Furthermore, natural proteins other than globin do not combine with oxyhæmatin or with reduced hæmatin to give compounds comparable with those of the hæmoglobin series. The only known example of a natural pigment parallel to hæmoglobin is Munro Fox's chlorocruorin.<sup>94</sup> In this pigment the prosthetic group contains iron, but the porphyrin differs from that of hæmoglobin. Neutral oxyhæmatin combines with a number of nitrogenous derivatives, including *denatured* globin, nicotine, pyridine, and histidine, to give a series of compounds which Keilin has called parahæmatins.<sup>95</sup> It would appear that helicorubin, the pigment found in the liver and gut of pulmonate molluscs and in the liver of the crayfish, belongs to this group of substances. Alkaline oxyhæmatin does not combine with nitrogenous substances.

*Hæmochromogen.*—A highly important group of compounds is encountered when we consider those substances formed by reduced hæmatin interacting with nitrogenous compounds. We have already seen that when the nitrogenous substance is *natural* globin, reduced hæmoglobin is obtained, but with *denatured* globin a substance of a much lower degree of molecular complexity, namely hæmochromogen, results. Many other nitrogenous compounds in addition to globin may enter into combination with reduced hæmatin: amongst them are to be numbered other proteins such as denatured albumin and globulin, glycine, nicotine, pyridine, piperidine, hydrazine, and ammonia. We owe to Anson and Mirsky<sup>96</sup> the general conceptions of the relationships of these compounds to hæmoglobin, and of the molecular structure of the hæmochromogens. The latter all differ markedly from reduced

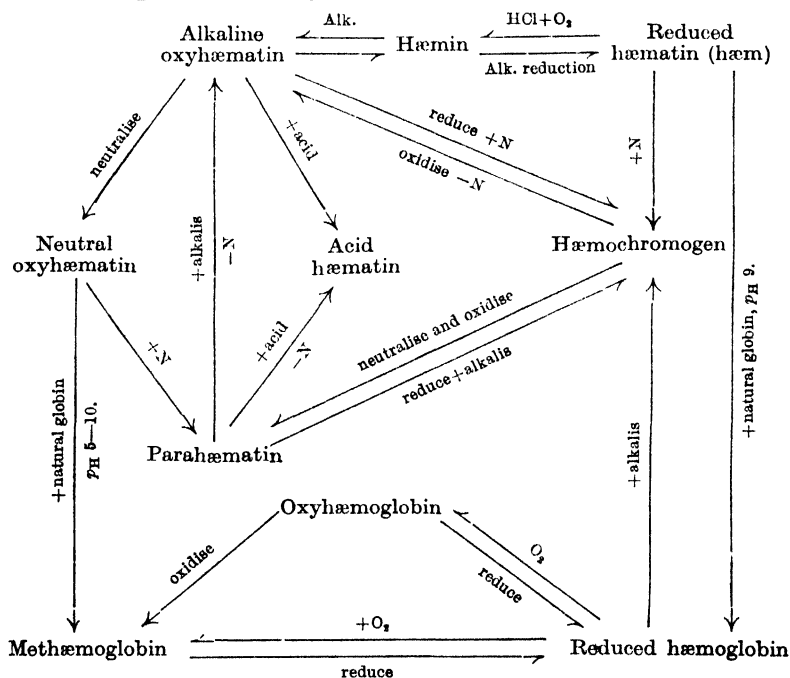
<sup>94</sup> *Proc. Roy. Soc.*, 1926, *B*, **99**, 199; *A.*, 1926, 313.

<sup>95</sup> *Ibid.*, 1926, *B*, **100**, 129; *A.*, 1926, 857.

<sup>96</sup> *Ann. Reports*, 1925, **22**, 237.

hæmatin in solubility, colour, absorption spectrum, and in the compounds which they form with carbon monoxide. The hæmochromogens oxidise readily in the air, and in an alkaline medium they dissociate into their nitrogen compound and hæmatin, or, as Anson and Mirsky called it, hæm. Keilin has shown that in a neutral solution they do not dissociate but are transformed into parahæmatins, which we have seen to be compounds of oxyhæmatin.

Until the work of Anson and Mirsky was published, general acceptance was accorded to the idea that what were then called hæmatin and hæmochromogen comprised the protein-free prosthetic group of hæmoglobin in an oxidised and a reduced condition respectively. Anson and Mirsky, in the work which has just been outlined above, clearly established the true nature of hæmochromogen as a compound of globin (or, in the case of artificial hæmochromogens, of some other nitrogenous substance), but they were mistaken in stating that hæmatin was also a globin compound. It was for these reasons, one correct, the other a mistake, that the term hæm was introduced by them to designate the free prosthetic compound, and a good deal of confusion has since resulted.



*Scheme showing relationship of the blood pigments. The expressions  $+N$  and  $-N$  are intended to indicate the addition or the removal of denatured globin or other nitrogenous compound.*

The reader will, however, find the position quite clear if he bears in mind the identity of Anson and Mirsky's hæm with reduced hæmatin. The cause of the original mistake was cleared up by Keilin when he showed that the alkaline hæmatins prepared from hæmogoblin and from hæmin crystals were identical and devoid of protein, whereas acid hæmatin prepared from hæmoglobin is a colloidal suspension of hæmatin, which is not united with globin, but is protected by the latter from precipitation. There is appended a scheme, modified slightly from one given by Keilin, which will be found helpful in tracing the relationships which we have discussed.

The term hæmochromogen in its modern usage is really a very wide one, since one may vary, not only the nitrogenous compound, but also the iron-porphyrin. It has been shown that only slight alterations in the characteristic absorption bands are produced when reduced hæmatin is combined with a series of nitrogen compounds, but, on the other hand, more marked differences result when the same nitrogen compound is combined with different porphyrins. Another factor which influences greatly the positions of the bands is the degree of dispersion of the hæmochromogen; with increasing molecular aggregation the bands become displaced towards the red end of the spectrum. Thus when a hæmochromogen is present both in solution and in a fine colloidal suspension, the liquid shows three absorption bands, formed of two superimposed spectra, comprising two  $\alpha$ -bands and one fused  $\beta$ -band.

*Cytochrome.*—In 1925 Keilin<sup>97</sup> showed that a very large number of aërobic plant and animal tissues when examined with a microspectroscope showed a series of bands similar to those of the hæmochromogens, and he established the origin of these bands as being due to a widespread respiratory pigment which he called cytochrome. These observations were confirmed and extended by Schumm<sup>98</sup> and by Euler, Fink and Hellström.<sup>99</sup> It became clear that cytochrome was in fact a porphyratin combined with a nitrogenous substance and showed a remarkable similarity to hæmochromogen. Keilin has shown that in reality cytochrome is a mixture of three hæmochromogens, or rather of the same hæmochromogen in three different physical states, each one of which contributes its characteristic  $\alpha$ - and  $\beta$ -bands to the complex four-band spectrum of the complete substance, bands *a*, *b*, and *c* being the three separate  $\alpha$ -bands, and band *d* the three fused  $\beta$ -bands. Under certain conditions these three hæmochromogens may become

<sup>97</sup> *Ann. Reports*, 1925, 22, 258.

<sup>98</sup> *Z. physiol. Chem.*, *loc. cit.* and p. 55; 1926, 154, 171, 314; 1927, 166, 1; A., 685.

<sup>99</sup> *Ibid.*, 1927, 169, 10; A., 993.

oxidised (in which case the bands disappear) or reduced independently of one another, so that the particular bands shown by cytochrome and also their relative intensities may vary with the conditions employed. There is also present in all cells which contain cytochrome free hæmatin, and the latter, combining under various conditions of oxidation and reduction with different nitrogen compounds, gives rise to the three hæmochromogen components of cytochrome, two differing in degree of dispersion and the third partly modified by the active process of oxidation and reduction.

The respiratory functions of cytochrome have been carefully studied by Keilin. The fact that the pigment is confined to aërobic organisms, and its behaviour in them, at once suggested that it is concerned with the utilisation of oxygen, either directly or in conjunction with an oxydase system. It has been shown that along with cytochrome there is found an oxydase<sup>1</sup> which can be detected by its capacity to form indophenol from dimethyl-*p*-phenylenediamine hydrochloride and  $\alpha$ -naphthol. It seems probable that this oxydase system is identical with the respiratory ferment described by Warburg,<sup>2</sup> which is present in yeast and cocci cells and is inhibited by carbon monoxide. Haldane<sup>3</sup> has shown a similar respiratory system to be present in the wax-moth and in cress plants, so that its distribution is probably a very wide one. Keilin has brought forward evidence to show that cytochrome, or at least two of its component hæmochromogens, is oxidised by this phenoloxydase and reduced by reductases or by other cellular constituents which become oxidised irreversibly. Cytochrome may therefore act as a "Hilfkatalyst" in the sense of Oppenheimer,<sup>4</sup> or as a respiratory chromogen acting either as a peroxydase or as a catalyst. It would therefore seem that in cytochrome there is revealed a considerable part of the complex system of oxidative cellular catalysts.

*The Porphyrins.*—There has been described a very large number of closely similar porphyrins and their derivatives obtainable from natural sources directly or by simple chemical transformations. It would seem probable that the tetrapyrrole compounds from which these are derived must be capable of existing in isomeric forms and of giving rise to a large number of simple substituted derivatives. The most striking recent advance in the study of these porphyrins, which fully justifies these suppositions, has been

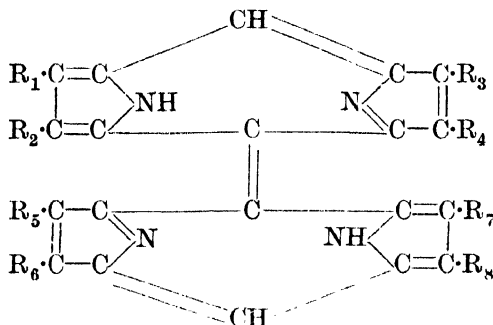
<sup>1</sup> *Nature*, 1927, **119**, 670; **A.**, 592.

<sup>2</sup> *Biochem. Z.*, 1926, **177**, 471; 1927, **189**, 354; **A.**, 1926, 1277; 1927, 1221.

<sup>3</sup> *Nature*, 1927, **119**, 352; **A.**, 375; *Biochem. J.*, 1927, **21**, 1068; **A.**, 1110.

<sup>4</sup> "Die Fermente und ihre Wirkungen," Leipzig, 1926.

the synthesis of ætioporphyrin, identical with Willstätter's ætioporphyrin from natural sources, by Fischer and Klarer,<sup>5</sup> and of isoætioporphyrin by Fischer and Halbig.<sup>6</sup> As a result of this achievement Fischer is able to make a more authoritative suggestion regarding the structure of ætioporphyrin, and therefore of porphyrins related to it, than has hitherto been possible. The suggested structure, which forms the basis of these and other porphyrins, is as follows :



The structure of ætioporphyrin as demonstrated by synthesis is obtained by substituting for  $R_1$ ,  $R_4$ ,  $R_5$ , and  $R_8$  the  $C_2H_5$  radical, and for  $R_2$ ,  $R_3$ ,  $R_6$ , and  $R_7$  the  $CH_3$  radical. On this basis, current views on the constitution of coproporphyrin are expressed by substituting for  $R_1$ ,  $R_4$ ,  $R_5$ , and  $R_8$  the group  $-CH_2 \cdot CH_2 \cdot CO_2H$ , and for  $R_2$ ,  $R_3$ ,  $R_6$ , and  $R_7$ ,  $-CH_3$ . The closely related uroporphyrin is similarly formulated by replacing each of the groups  $-CH_2 \cdot CH_2 \cdot CO_2H$  in the coproporphyrin formula by the dicarboxylic acid group  $-CH_2 \cdot CH(CO_2H)_2$ .

It is clear that from a tetrapyrrole nucleus of this type numerous isomeric and closely related porphyrins can be derived, and it is therefore not surprising that numerous representatives of the class are reported from time to time as occurring in nature. The subject is still in too complex a state of development to be suitable for review, but as illustrative of the type of investigation in progress may be cited the recent preparation of deuteroporphyrin by Fischer and Lindner.<sup>7</sup> This porphyrin has been obtained by fermenting fresh ox-blood spontaneously, or with yeast, an alkaline reaction being preserved throughout. Evidence is adduced of its constitution and this can be expressed by substituting as follows in the formula already given: for  $R_1$ ,  $R_4$ ,  $R_6$ , and  $R_7$ ,  $-CH_3$ , for  $R_3$  and  $R_5$ ,  $-H$ , and for  $R_2$  and  $R_8$ ,  $-CH_2 \cdot CH_2 \cdot CO_2H$ .

<sup>5</sup> *Annalen*, 1926, **448**, 178; *A.*, 1926, 962.

<sup>6</sup> *Ibid.*, p. 193; *A.*, 1926, 963.

<sup>7</sup> *Z. physiol. Chem.*, 1926, **161**, 17; *A.*, 1927, 262.

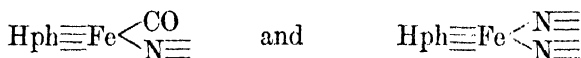
All these porphyrins are capable of forming the corresponding iron porphyratins, and Fischer and his co-workers have prepared synthetic *ætiohæmin* and *isoætiohæmin* from the corresponding synthetic porphyrins by treating the latter with ferric chloride and sodium acetate. The nature of these iron compounds has yet to be elucidated, but a recent important publication by Hill<sup>8</sup> gives some indication of their probable nature. *Hæmatoporphyrin* was prepared from pure *hæmin* and the former was then reconstituted by artificial means. The corresponding nickel and copper porphyratins were also prepared. Whereas the nickel and copper compounds still showed their typical two-band spectra, the iron compound resembled reduced *hæmatin* in showing only an ill-defined region of absorption. The *hæmochromogen* type of spectrum shown by compounds of *hæmatoporphyrin* with metals other than iron is shown by Hill not to be due to the presence of nitrogen compounds, and it is suggested that the property of forming *hæmochromogens* is limited to the iron-porphyrin compounds. On addition of denatured globin, pyridine, or ammonia the iron compound gave *hæmochromogen*. Thus the artificial iron-*hæmatoporphyrin* showed the same behaviour as *hæmin* prepared directly from blood. Nickel and copper *hæmatoporphyrins* showed no change on the addition of denatured globin. The iron compound of *hæmatoporphyrin* thus behaved exactly as *hæmatin* and on reduction did not give the *hæmochromogen* spectrum shown by other metallic derivatives of *hæmatoporphyrin*, unless some nitrogen compound was present. It is deduced from these observations that *hæmochromogen* is simply the ferrous compound of the porphyrin, corresponding with the bivalent copper and nickel compounds, together with a nitrogenous substance. Since iron *hæmatoporphyrin* gives a different spectrum according to the reagents present when the pigment is reduced in alkaline solution, and since this property is not shared by any other porphyratin so far examined it is inferred that the iron atom alone confers on the pigment the property of forming molecular compounds with a large variety of substances when the pigment is in the reduced state.

From quantitative measurements of the combination of pyridine with reduced *hæmatin*, Hill has shown that in carbon monoxide-*hæmochromogen* one nitrogen-containing molecule is replaced by CO, there being two such nitrogenous molecules in *hæmochromogen* itself. By adding the nitrogen compound to CO-reduced *hæmatin*, one molecule of the former is taken up, and by adding excess of the nitrogen compound, the CO is displaced by the taking up of another molecule of the nitrogen compound and *hæmochromogen*

<sup>8</sup> *Proc. Roy. Soc.*, 1926, B, 100, 419; A., 1927, 65.



is formed. These changes occur when any nitrogen compound is used which gives a typical hæmochromogen, including denatured globin itself. Since iron is the only element in combination with the pigment which causes it to have the property of forming hæmochromogen, it is simplest to assume that the nitrogen and carbon monoxide are directly co-ordinated with the iron, which has a co-ordination number of 6. The general formulæ for a carbon monoxide-hæmochromogen and for hæmochromogen are therefore written thus (Hph being hæmatoporphyrin and N the nitrogenous substance) :



The chief objection to this view, as Hill himself points out, is the fact that the carbon monoxide compound of reduced hæmatin, without pyridine or other nitrogen compound, contains not two molecules, but only one molecule of carbon monoxide. The formula can, however, be written :



where X is either another molecule of the complex or a molecule of solvent. It may be added that there is evidence that reduced hæmatin combines with itself to form large molecules in the absence of the specific reagents mentioned, because of its insolubility and the slowness with which it reacts with such reagents.

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JOHN PRYDE.

## CRYSTALLOGRAPHY.

A REPORT of this nature cannot claim to deal exhaustively with all the work on crystallography, of direct or indirect interest to chemistry, which has appeared during the year. It is necessary to limit the scope, so as to be able to deal adequately with the subjects chosen. We have selected for special treatment the work on the influence of atomic size and chemical constitution on the structure of crystals, which has been so admirably summarised in the papers of V. M. Goldschmidt, and also the work on the structure of alloys, which, in the hands of Westgren, Phragmén, and others, has made considerable advances since it was last dealt with in these Reports.

Of great interest to all workers on crystallography is the report by P. P. Ewald and C. Hermann on all crystal structures investigated by X-ray methods from 1913 to the end of 1926, which is at present appearing in serial form in the *Zeitschrift für Kristallographie*. In Vol. 65, which is just completed, the elements and a number of binary compounds have been dealt with. The descriptions of the structures, given in considerable detail, are very clear and extensively illustrated. The whole, when completed, will form a most valuable compendium.

### *Sizes of Ions in a Crystal Lattice.*

During the last few years a large amount of work has been done on the sizes of the atomic domains in the crystal state. The idea of a definite volume associated with a given atom or ion, which, in compounds of the same type, it always occupies, is becoming increasingly important as an aid to crystal analysis. For an account of the work which has been done in this subject up to 1926 reference may be made to the section entitled "Grösse und Bau der Moleküle" by H. G. Grimm in Geiger and Scheel's *Handbuch der Physik*, XXII, p. 499.

Quite recently a new estimate of ionic radii has been made by L. Pauling,<sup>1</sup> who bases his work on the idea that the dimensions of an ion are conditioned by the radius of the outer electron shell, and that this in its turn, for ions of similar structure, is inversely pro-

<sup>1</sup> *Proc. Roy. Soc.*, 1927, [A], **114**, 181; **A.**, 394; *J. Amer. Chem. Soc.*, 1927, **49**, 765; **A.**, 399.

portional to the effective nuclear charge acting on that shell. He employs a method based on the wave mechanics to calculate this effective nuclear charge, and is thus able to obtain the ratio of the radii of pairs of ions. To get the actual sizes, he uses as his starting point the experimental interionic distances, giving the sum of the two "radii," in NaF, KCl, RbBr, and CsI, together with an assumed value for Li of 0.60 Å. obtained from the experimental distance in lithium oxide. We give in Table I a number of the ionic radii so calculated, compared with the empirical values given by V. M. Goldschmidt.<sup>2</sup> It will be seen that the agreement on the whole is very good.

TABLE I.  
(Ionic radii, in Ångström units.)

	O <sup>-2</sup> .	F <sup>-1</sup> .	Ne.	Na <sup>1</sup> .	Mg <sup>2</sup> .	Al <sup>3</sup> .	Si <sup>4</sup> .	P <sup>5</sup> .	S <sup>6</sup> .
Goldschmidt	1.32	1.33	1.52	0.98	0.78	0.57	0.39	0.3—0.4	0.34
Pauling .....	1.40	1.36		0.95	0.65	0.50	0.41	0.34	0.29

The values used for O<sup>-2</sup> and F<sup>-1</sup> by Goldschmidt are those deduced by J. A. Wasastjerna.<sup>3</sup> Since, from empirical data from crystals we cannot obtain the actual radius, but only the sum of two radii, we must assume the radius of at least one ion, and Wasastjerna's values are here taken as the starting point. The above table shows only a few values; many more are given in the papers to which reference has been made.

*The Relation between Crystal Structure and the Nature of the Atoms taking Part in it.*

In a series of papers briefly mentioned in last year's Report, V. M. Goldschmidt<sup>2</sup> has given an interesting survey of the different types of crystal structure formed by the simpler compounds, and of the conditions under which one or other of these types occurs. Although many of the ideas emphasised have been implicit in a good deal of the work on crystal structure, they are summarised very clearly and much new matter is included. The whole is based upon a mass of experimental work, most of which has been carried out in Goldschmidt's laboratory at Oslo. Reference may be made to a good summary of the work, the material of a lecture by Goldschmidt<sup>4</sup> to the German Chemical Society. Goldschmidt points out that purely geometrical considerations, based on the idea of an ionic radius characteristic of each ion, play a very important part in determining which type of structure is formed, particularly

<sup>2</sup> "Geochemische Verteilungsgesetze der Elemente," VII and VIII, *Norske Videnskaps-Akad. (Mat. Nat. Kl.)*, 1926, Nos. 2 and 8.

<sup>3</sup> *Z. physikal. Chem.*, 1922, **101**, 193; *A.*, 1922, ii, 491.

<sup>4</sup> *Ber.*, 1927, **60**, [B], 1263; *A.*, 611.

when the constituents are simple ions having the inert-gas structure. It is supposed that one important condition for the stability of an ionic structure is that anion and cation may touch one another. The number of ions of type X which can surround and touch an ion of type A depends on the ratio of the radii of A and X, supposing each ion to be a sphere with a definite radius. In Table II, which is taken from Goldschmidt's work, are shown, in the first column the number of ions X which are supposed to surround and touch an ion A; in the second the number and arrangement of the ions X around A, and in the third the smallest value of the ratio of the radii of the ions,  $R_A/R_X$ , which is permissible in order that such an arrangement may be possible. It is to be emphasised that the essential point is the contact of X and A.

TABLE II.

*Arrangement of X Ions around the Ion A.*

Number of ions X.	Arrangement of X.	Limiting ratio $R_A/R_X$ .
3	At corners of an equilateral triangle.	0.15
4	At corners of a tetrahedron (ZnS)	0.22
4	At corners of a square in the plane of A.	0.41
6	Along the edges of a cube, A at corner (NaCl); or at corners of an octahedron.	0.41
8	At corners of a cube with A in the middle.	0.73

We may now consider the different types of compound AX and  $AX_2$  with respect to the co-ordination of the ions one to another. In the zinc sulphide lattice, each ion has four neighbours of the opposite kind, in NaCl and NiAs, six, and in CsCl, eight.

For lattices of the type  $AX_2$  there are twice as many ions of the opposite sign around A as there are around X. For the different types of lattice the numbers are as follows:  $CO_2$ , 2 and 1;  $SiO_2$ ,  $Cu_2O$ , 4 and 2;  $TiO_2$  (rutile or anatase),  $CdI_2$ ,  $MoS_2$ , 6 and 3;  $CaF_2$  (fluorite), 8 and 4.

Now, so long as we are dealing with simple ionic structures, it is found that the type of lattice formed by a pair of ions can generally be predicted by ascribing to each ion one of the radii discussed in the preceding section, and taking into consideration the limiting ratios of the radii for different types of co-ordination. A few of the many examples given may be quoted.

Of the fluorides of the bivalent metals,  $MgF_2$ ,  $NiF_2$ ,  $CoF_2$ ,  $FeF_2$ ,  $ZnF_2$ , and  $MnF_2$  have the rutile structure with co-ordination numbers 6 and 3, whereas  $CdF_2$ ,  $CuF_2$ ,  $HgF_2$ ,  $SrF_2$ ,  $PbF_2$ , and  $BaF_2$  have the fluorite structure with co-ordination numbers 8 and 4. The series as given is arranged in ascending order of  $R_A/R_X$ . The value of the ratio for  $MnF_2$  is 0.68, and for  $CdF_2$  0.77, whereas the limiting value of the ratio for the transition from the one type of co-ordin-

ation to the other is seen from Table II to be 0.73. Further, the oxides, sulphides, selenides, and tellurides of Mg, Ca, Sr, and Ba all have the rock-salt structure (co-ord. number 6) except MgTe, which has the wurtzite structure (co-ord. number 4). For the rock-salt structure the ratio  $R_A/R_X$  must be between 0.41 and 2.45; MgTe is the only compound of this whole series in which the ratio falls outside these limits, its value being 0.37. The atomic radii cannot be treated as exactly constant. There is a definite decrease as the co-ordination number decreases, and thus the limits are only approximate; but there is no doubt that for a large class of compounds purely geometrical considerations of this kind are more important than chemical considerations in determining the type of crystal structure.

Geometry is not, however, the only factor. If one of the ions is much more readily polarisable than the other, so that it tends to become an electric dipole under the action of a field, this may have great influence on the actual structure, although geometrical considerations will remain as an important factor.

An example is given by the cadmium iodide lattice. Each cadmium ion lies between six iodine ions, and the iodine has three cadmium ions as nearest neighbours. The crystal forms sheets composed of two layers of iodine atoms held together by the cadmium in between them. The iodine ions will be strongly polarised by the cadmium ions. Each sheet is a very rigid structure. Adjacent sheets, however, are only lightly held together so that the crystal has a very perfect cleavage. Lattices of this type have been termed "Schichtengitter," or "layer lattices," by F. Hund.<sup>5</sup> The condition for such a layer lattice appears to be that one of the constituents should be readily polarisable. This is illustrated by the following fact. Cadmium fluoride has the fluorite structure. If we replace F' by OH' we get a layer lattice.<sup>6</sup> Geometrically, OH' occupies about the same space as F', but it is a natural dipole and so the layer lattice is formed. Similarly, if in SnO<sub>2</sub> or TiO<sub>2</sub> we replace O'' by S'', which is more readily polarisable, the rutile lattice changes to a layer lattice of the cadmium iodide type.<sup>7</sup>

The lattices so far considered are of the purely ionic type, although modified by polarisation effects. We must now consider briefly some lattices which are certainly not ionic. One of the types of AX lattice is typified by nickel arsenide, NiAs. The arsenic atoms are here nearly in hexagonal close-packed array. The nickel atoms lie in the gaps in the structure, between six arsenic atoms.

<sup>5</sup> *Z. Physik*, 1925, **34**, 833; *Physikal. Z.*, 1925, **26**, 682; *A.*, 1925, ii, 1132.

<sup>6</sup> G. Natta, *Atti R. Accad. Lincei*, 1925, [vi], **2**, 495; *A.*, 1926, 228.

<sup>7</sup> A. E. van Arkel, *Physica*, 1924, **4**, 286; *A.*, 1925, ii, 749.

The series of sulphides, selenides, and tellurides of Ca, Mn, Fe, Co, and Ni show a transition from the NaCl structure to the NiAs structure with increasing atomic number of either ion. There is at the same time a considerable decrease in the interatomic distance below that appropriate to an ionic lattice of the rock-salt type for the same elements. One remarkable fact about lattices of this type is that more or less free isomorphous replacement seems to take place between the components. For example, ferrous sulphide and sulphur form an isomorphous mixture in which the excess of sulphur appears to be able to replace iron in a lattice of the NiAs type.<sup>8</sup> Goldschmidt and his co-workers found the same thing for CoSe, MnSb, and FeSb, and suggest that the formulæ of such compounds might better be written  $\text{Fe}_x\text{Sb}_y$ , and so on. Such lattices seem only to be formed when the metallic atom belongs to the series from scandium to nickel in which there is a deficiency of electrons in the *M*-group. Goldschmidt goes so far as to suggest that part of the negative charge of the anion either directly or indirectly tends to make good this deficiency. Assuming that a deficiency in an inner electron group in the cation, and a large and readily polarisable anion are the essentials for this type of structure, Goldschmidt argues that compounds of metals of the platinum group with readily polarisable ions should show the NiAs structure. This has been verified for the compound PtSn.

Another type of lattice of great interest is that in which each component has four neighbours, the zinc blende or wurtzite lattice. The geometrical condition for such a lattice is a ratio of radii between 0.22 and 4.5, but there seems to be a further condition, which was pointed out by M. L. Huggins<sup>9</sup> and by H. G. Grimm and A. Sommerfeld.<sup>10</sup> The condition is that the element A must be as many places (up to three) in the periodic table before one of the elements, C, Si, Ge, Sn, Pb, as the element X is beyond it. The sum of the outer electrons of the two components must therefore be eight. The lattice which is so formed is not a simple ionic lattice, as can be seen by studying the atomic distances in the series given in Table III, which was investigated by Goldschmidt. Grey tin forms a lattice of the diamond type; the other compounds in the series are formed

TABLE III.

Atomic number.	Compound.	Lattice constant.	Atomic distance.
50,50	SnSn	6.46 Å.	2.79 Å.
49,51	InSb	6.452 „	2.793 „
48,52	CdTe	6.463 „	2.799 „
47,53	AgI	6.491 „	2.811 „

<sup>8</sup> N. Alsén, *Geol. Förel. Förel.*, 1925, **47**, 19.

<sup>9</sup> *Physical Rev.*, 1926, [ii], **27**, 286; **A.**, 1926, 458.

<sup>10</sup> *Z. Physik*, 1926, **36**, 36; **A.**, 1926, 560.

by increasing the atomic number of one component above that of tin and decreasing that of the other by the same amount below it, so that the sum of the atomic numbers remains 100. The most remarkable thing about the series of compounds so formed, all of which crystallise on the zinc blende (diamond-like) or wurtzite lattices, is the constancy of the interatomic distance. We should not get this constancy in a similar series of compounds of the sodium chloride type. If we take another of the quadrivalent elements as the starting point, we get another series, with a different constant atomic distance. We must refer the reader to Goldschmidt's work for a complete table of such compounds. The lattice here is not an ionic lattice, neither in all probability is it, strictly speaking, atomic or molecular. Goldschmidt concludes that the individuality of the single elements matters but little. There seems to be a common structure of the whole crystal, the dimensions of which are controlled almost entirely by the total number of negative charges, and scarcely at all by the distribution of the positive charges on the single atomic nuclei. In the next section we shall see that similar considerations are true for alloys and intermetallic compounds. Indeed, both in the NiAs and the wurtzite types of structure many of the crystals have a metallic lustre and appearance. Such crystals may represent a transition stage between the non-metallic compound and the true metals.

#### *The Crystal Structure of Alloys.*

In a previous Report<sup>11</sup> some account was given of the work of A. Westgren and G. Phragmén on the copper-zinc, silver-zinc, and gold-zinc alloys. These authors have extended this work, and have found that four types of crystal structure are common to each of these series of alloys, and to certain other alloy systems.<sup>12</sup> These are (1) face-centred cubic, (2) body-centred cubic, (3) hexagonal close-packed, and (4) a complex cubic structure.

The face-centred structure is the structure of the pure metals, copper, silver, and gold. When small quantities of zinc, aluminium, or tin are added to these metals no change is produced in the type of crystal structure. The atoms of the one kind are replaced by those of the other kind, atom by atom, producing an arrangement which, so far as X-ray analysis can tell, is indistinguishable from that of a pure metal. Such an arrangement is a solid solution, and is characterised by the fact that atoms of different kinds behave in an identical

<sup>11</sup> *Ann. Reports*, 1925, **22**, 253.

<sup>12</sup> *Z. Metallk.*, 1926, **18**, 279; *A.*, 1926, 1084. Compare also E. A. Owen and G. Preston, *Proc. Physical Soc. London*, 1923, **36**, 49; M. Andrews, *Physical Rev.*, 1921, [ii], **18**, 245.

manner, being distributed at random throughout the structure. This arrangement is only possible when the alloy contains large proportions of the parent metal, *i.e.*, the metal which has the same structure as the solid solution. With greater quantities of the foreign element, the structure breaks down and the atoms proceed to arrange themselves in quite a different way.

One of these alternative structures is a peculiar complex cubic arrangement, which possesses many remarkable features. This arrangement is formed by copper, silver, or gold alloyed with zinc, and by copper alloyed with aluminium or tin. Although the structures are very similar in each case, there is actually a progressive increase of complexity in passing from the zinc alloy to the aluminium alloy, and from the latter to the tin alloy.

The arrangement of the atoms in the copper-zinc alloy has been determined.<sup>13</sup> The type of co-ordination is remarkable, each atom being surrounded by 11, 12, or 13 neighbours at approximately equal distances, each neighbouring atom being as far as possible of the opposite sort. This structure is stable over a wide range of concentrations, the zinc content varying from a value corresponding to the formula  $\text{Cu}_5\text{Zn}_8$  to one corresponding to  $\text{Cu}_4\text{Zn}_9$ . The atoms actually appear to be divided in a manner that would correspond to the formula  $\text{Cu}_5\text{Zn}_8$ , any excess of zinc atoms replacing individual copper atoms in a random manner, so that the phase is a solid solution based on the compound  $\text{Cu}_5\text{Zn}_8$ . The same is true of the silver and gold alloys, which are based on the formulæ  $\text{Ag}_5\text{Zn}_8$  and  $\text{Au}_5\text{Zn}_8$ , respectively.

The element manganese,<sup>14</sup> in the  $\alpha$ -form, bears a striking resemblance to these complex cubic alloys. It contains 58 atoms in a cube of approximately the same size as the unit cube of the alloy, and there is a somewhat similar disposition of atoms. The distance between neighbouring atoms, however, varies considerably. All these facts seem to indicate that  $\alpha$ -manganese contains atoms which are in some way different in character, so that the structure is akin to that of an alloy rather than to that of a true element.

The complex cubic alloys of zinc with copper, silver, and gold all have compositions corresponding to the same atomic percentages, so that the resemblance is in this case a typical instance of isomorphism, and presents no unusual features when viewed from the normal chemical standpoint. The relationship between the alloys of copper with zinc, aluminium or tin is, however, less simple. As the valency of the replacing atom (Zn, Al, or Sn) increases, phases corresponding to the complex structure become richer in copper.

<sup>13</sup> A. J. Bradley and J. Thewlis, *Proc. Roy. Soc.*, 1926, [A], **112**, 678; **A.**, 1926, 1084.

<sup>14</sup> *Idem, ibid.*, 1927, [A], **115**, 456; **A.**, 814.



A similar shift in composition was found in the case of the hexagonal structures which Westgren and Phragmén investigated. They traced the existence of a hexagonal close-packed type of structure in binary alloys of silver with zinc, aluminium, or tin. The silver content of the alloy is found to be greater for trivalent aluminium than for bivalent zinc, and still greater for quadrivalent tin.

Westgren and Phragmén suggest that the ratio of the number of valency electrons to the number of atoms is a significant factor in deciding the nature of the atomic arrangement in such cases as these. This is by no means unlikely, for W. Hume-Rothery<sup>15</sup> has already pointed out that the three alloys the empirical compositions of which may be represented by the formulæ  $\text{CuZn}$ ,  $\text{Cu}_3\text{Al}$ , and  $\text{Cu}_5\text{Sn}$  have very similar microstructures, and has suggested that this is due to the fact that the ratio of valency electrons to atoms is in each case 3 : 2. He further suggests that these alloys all possess the body-centred cubic structure, which Westgren and Phragmén have shown to be typical of the  $\beta$ -phases of the alloys copper-zinc, silver-zinc, and gold-zinc. These alloys correspond to the formulæ  $\text{CuZn}$ ,  $\text{AgZn}$ , and  $\text{AuZn}$ , so that an arrangement of the atoms as in the case of  $\text{CsCl}$  is possible. This caesium chloride structure has also been shown by E. A. Owen and G. D. Preston<sup>16</sup> to hold good in the case of the analogous alloys  $\text{AuZn}$  and  $\text{AgMg}$ .

Two recent papers by C. H. Johansson and J. O. Linde,<sup>17</sup> who have tried to establish a relationship between crystal structure and electrical conductivity, are of great interest. Copper can be alloyed with gold, platinum, or palladium in all proportions, giving a series of alloys which are ideal solid solutions, consisting only of a single face-centred cubic lattice with a random distribution of the constituent elements. In any such series of alloys the electrical conductivity decreases continuously with a rising percentage of the substituent metal, until it finally reaches a minimum and then steadily rises as the substituent metal becomes the dominant constituent. Johansson and Linde show, however, that, when the constituents occur in certain definite proportions, prolonged annealing at temperatures below  $400^\circ$  produces a remarkable increase in the electrical conductivity of the alloys. At the same time, new lines appear on the X-ray photographs obtained from the alloys, which show quite definitely that a rearrangement of the atoms has taken place, and that the constituent elements are no longer distributed in a haphazard way. For example, the alloys of copper with gold,

<sup>15</sup> *J. Inst. Metals*, 1926, **35**, 313; *A.*, 1926, 356.

<sup>16</sup> *Phil. Mag.*, 1926, **2**, 1266; *A.*, 1927, 96.

<sup>17</sup> *Ann. Physik*, 1925, **78**, 439; 1927, **82**, 449; *A.*, 1926, 112; 1927, 400. Compare also E. C. Bain, *Chem. Met. Eng.*, 1923, **28**, 21.

platinum, or palladium show a face-centred cubic arrangement, with, in general, a random distribution of the elements; but with alloys containing 75 atoms % of copper, rearrangement takes place on annealing in such a way that the atoms at the centres of the cube faces are copper, and those at the cube corners the other metal. The increased conductivity and the regular arrangement of atoms invariably occur together. Reheating at a temperature above  $400^{\circ}$  removes both the extra conductivity and the new X-ray lines. Similar rearrangement takes place when the alloys contain 50 atoms % of each constituent. The crystal structures differ, however, with the different elements, the gold alloy being tetragonal, the platinum alloy trigonal, and the palladium alloy cubic, with a caesium chloride type of structure.

According to G. Tammann,<sup>18</sup> any solid solution may be expected to produce a regularly arranged structure if annealed under suitable conditions; but the work of Johansson and Linde seems to show that such rearrangement is exceptional and can only occur at certain concentrations, the resulting structures being in fact intermetallic compounds. From this point of view, an intermetallic compound may be merely a special case of a solid solution, in which the random distribution has been replaced by a more regular distribution of the atoms of different types.

### *Crystal Structures of Metallic Elements.*

G. Asahara and T. Sasahara<sup>19</sup> have investigated the crystal structures of metallic thallium, using single crystals prepared by electrolysis. They find the structure to be hexagonal close-packed, thus confirming the work of G. R. Levi,<sup>20</sup> which had been questioned by K. Becker.<sup>21</sup>

The crystal structure of metallic gallium<sup>22</sup> has been found to be tetragonal, containing eight atoms per unit cell. There are two parameters which have not been determined.

F. Simon and E. Vohsen<sup>23</sup> have determined the crystal structure of the alkali metals Na, K, Rb, and Cs and find them all to be body-centred cubic. The result for potassium conflicts with that given by V. M. Goldschmidt, who finds it to be tetragonal.

<sup>18</sup> "Lehrbuch der Metallographie" (Leipzig), 2nd edn., 1921, p. 329.

<sup>19</sup> *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1926, **5**, 79, 82; **A.**, 1927, 814.

<sup>20</sup> *Cim.*, 1924, **1**, 1; *Z. Physik*, 1927, **44**, 603; **A.**, 1013.

<sup>21</sup> *Ibid.*, **45**, 450; **A.**, 1129.

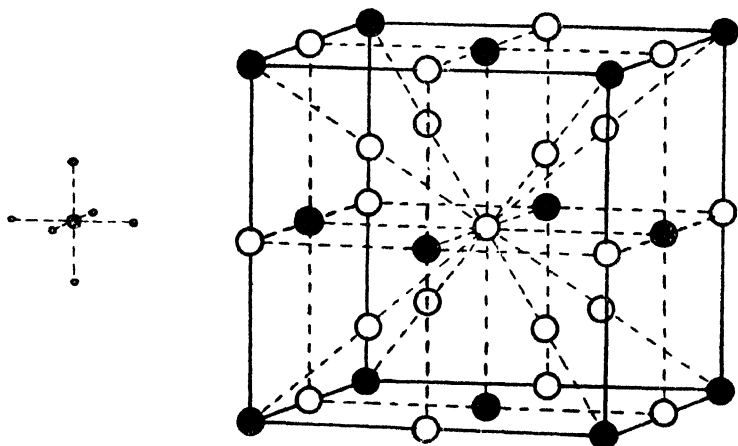
<sup>22</sup> F. M. Jaeger, P. Terpstra, and H. G. K. Westenbrink, *Proc. K. Akad. Wetensch. Amsterdam*, 1926, **29**, 1193; **A.**, 1927, 297.

<sup>23</sup> *Naturwiss.*, 1927, **15**, 398.

*Inorganic Crystals.*

*Co-ordination Compounds.*—The present state of the chemical theory of the nature of the atomic linkage in co-ordination compounds was summarised by N. V. Sidgwick in his Presidential Address to the Chemistry Section of the British Association in September 1927. The investigation of these compounds by *X*-ray methods is a matter of difficulty, since, owing to their complexity, the detailed elucidation of their structures is limited to those of high crystallographic symmetry; but enough information has already been obtained to support the general conclusions as to the stereochemistry of co-ordination compounds originally put forward by Werner. The following compounds have been examined.

FIG. 1.



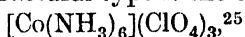
*Structure of  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ , showing unit cell.* The large open circles represent iodine atoms, the large black circles  $\text{Co}(\text{NH}_3)_6$  groups. The partial detail of these groups is shown in the smaller diagram. The small black circle represents the cobalt atom, the small open circles  $\text{NH}_3$  molecules.

*Hexa-amminocobaltic iodide,  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ .*<sup>24</sup> The crystal is cubic, the unit cell of side 10.88 Å. containing four molecules. The atomic positions in the unit cell are shown in Fig. 1, from which it will be clear that the structure may be regarded as built on a lattice which combines the NaCl and  $\text{CaF}_2$  lattices. The lattice points accommodate iodine atoms and co-ordination groups  $\text{Co}(\text{NH}_3)_6$ . One set of iodine atoms and the  $\text{Co}(\text{NH}_3)_6$  groups form a rock-salt lattice, whilst the other two sets of iodine atoms form with the same groups the  $\text{CaF}_2$  lattice. The ammonia molecules are arranged

<sup>24</sup> R. W. G. Wyckoff and T. P. McCutcheon, *Amer. J. Sci.*, 1927, [v], 13, 223; A., 400; H. Hentschel and F. Rinne, *Math.-Phys. Kl. Sächs. Akad.*, 1927, 79, 1; H. Meisel and W. Tiedje, *Z. anorg. Chem.*, 1927, 164, 223; A., 923.

octahedrally about the cobalt atom, as anticipated in the co-ordination theory. This type of composite lattice is of frequent occurrence, and reference is made to it elsewhere in the Report.

Of exactly similar structural type is the compound



the side of the unit cell of the cubic crystal having the length 11.39 Å. In this crystal, the oxygen atoms are arranged in fours about the chlorine atom, the perchlorate groups replacing the iodine atoms in Fig. 1.

An examination of  $(\text{NH}_4)_2\text{PbCl}_6$ ,<sup>26</sup> cubic ( $a = 10.14$  Å.), shows the unit cell to contain four molecules. The structure is of the  $\text{CaF}_2$  type in which calcium is replaced by the co-ordination group  $\text{PbCl}_6$ —each lead atom being surrounded by 6 chlorine atoms—and fluorine by the ammonium group. The structure is thus similar to that of the analogous salts  $\text{K}_2\text{PtCl}_6$  and  $\text{K}_2\text{SnCl}_6$ .

Of similar type, with obvious structural substitutions, are  $[\text{Co}(\text{NH}_3)_6]\text{I}_2$ ,<sup>27</sup>  $\text{Cs}_2\text{GeF}_6$ ,<sup>28</sup> and  $[\text{N}(\text{CH}_3)_4]_2\text{PtCl}_6$ .<sup>29</sup> Further examples of co-ordination compounds occur in later sections.

*Water of Crystallisation.*—Owing to the complexity of hydrated compounds in general, they have not received much attention in X-ray crystallography. E. J. Cuy<sup>30</sup> discusses the tendency of simple compounds to form hydrates and ammoniates, and the stability of such hydrates; he concludes that the question depends on the relative sizes of the ions forming the original compound.

With the idea of examining the geometrical significance of water in hydrated compounds, S. B. Hendricks and R. G. Dickinson<sup>31</sup> have determined the crystal structures of ammonium, potassium, and rubidium cupric chloride dihydrates ( $\text{R}_2\text{CuCl}_4 \cdot 2\text{H}_2\text{O}$ ). The crystals, which are tetragonal, have two molecules in the unit cell. The structure is of the calcium fluoride type (the unit cell is almost cubic), in which copper takes the place of calcium and R that of fluorine. Four chlorine atoms and two  $\text{H}_2\text{O}$  molecules are arranged octahedrally about each copper atom, thus forming a cupric chloride dihydrate co-ordination group. The group is, however, somewhat distorted, the two pairs of chlorine atoms involved being at different

<sup>25</sup> R. W. G. Wyckoff, S. B. Hendricks, and T. P. McCutcheon, *Amer. J. Sci.*, 1927, [v], **13**, 388; **A.**, 502.

<sup>26</sup> R. W. G. Wyckoff and L. M. Dennis, *ibid.*, 1926, [v], **12**, 503; **A.**, 1927, 97.

<sup>27</sup> H. Hentschel and F. Rinne, *Math.-Phys. Kl. Sächs. Akad.*, 1927, **79**, 1.

<sup>28</sup> R. W. G. Wyckoff and J. H. Müller, *Amer. J. Sci.*, 1927, [v], **13**, 347; **A.**, 503.

<sup>29</sup> M. L. Huggins, *Physical Rev.*, 1926, [ii], **27**, 638; **A.**, 1927, 1014.

<sup>30</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 201; **A.**, 191.

<sup>31</sup> *Ibid.*, p. 2149; **A.**, 1013.

distances from the copper atom. This distortion is regarded as corresponding to lack of stability in the co-ordination group.

O. Hassel and J. R. Salvesen<sup>32</sup> have examined a series of hetero-polar hexahydrates of the type  $MG_6LR_6$  where G and R may be  $H_2O$  and halide, respectively. Thus, in the case of zinc fluosilicate ( $ZnSiF_6 \cdot 6H_2O$ ), the structure is such that one set of ions representing a co-ordination group ( $Zn \cdot 6H_2O$ ) occupies the corners of a rhombohedron of angle  $96^\circ$ , the other complex,  $SiF_6$ , being at the centre of the rhomb. This rhomb is not, however, the true unit cell; apparently the octahedral arrangements of the  $H_2O$  molecules and fluorine atoms about the zinc and silicon respectively are such as to cause the true unit cell to be four times that of the rhomb just mentioned, and the final rhombohedral angle to be  $112^\circ$ . In addition to this series of compounds, the following were found to possess the same structure:  $[Co(NH_3)_6]Co(CN)_6$ ,  $[Co(NH_3)_5 \cdot H_2O]Co(CN)_6$ ,  $[Co(NH_3)_5 \cdot H_2O]Fe(CN)_6$ ,  $[Co(NH_3)_4 \cdot (H_2O)_2]Co(CN)_6$ .

J. M. Cork<sup>33</sup> has recently re-investigated the structure of the alums,  $KCr(SO_4)_2 \cdot 12H_2O$  and  $RAl(SO_4)_2 \cdot 12H_2O$ , where R is in turn  $(NH_4)$ , K, Rb, Cs, and Tl. The unit cell is cubic, of average side  $12.2 \text{ \AA}$ ., and contains four molecules; the cell dimensions vary little throughout the series. The structure may be regarded as being built on a distorted form of the composite lattice illustrated in Fig. 1. Each metal atom is symmetrically surrounded by six molecules of water, and each sulphur atom by four oxygen atoms. The sulphur atoms lie on the trigonal axes of the cell nearer to the trivalent metal than to the univalent metal.

*Mixed Crystals.*—Several papers have recently appeared on the character and conditions of formation of mixed crystals, but there is still considerable doubt as to the distribution of the constituent atoms in such crystals. The possibility that a mixed crystal is a composite of pure crystals of the two constituents is unlikely, since the presence of two different lattices would be revealed by X-rays. Objections of a theoretical nature are put forward by H. G. K. Westenbrink<sup>34</sup> against the suggestion that isomorphous substitution takes place atom by atom in a perfectly regular manner. G. Lunde<sup>35</sup> suggests that perfect mixture of the constituents occurs, but that the manner of atomic replacement is purely arbitrary and without regularity. The general conclusions to be drawn from the experimental results appear to be as follows:

(a) Mixed crystals may be formed from constituents whose

<sup>32</sup> *Z. physikal. Chem.*, 1927, **128**, 345; **A.**, 1014.

<sup>33</sup> *Phil. Mag.*, 1927, **4**, 688.

<sup>34</sup> *Rec. trav. chim.*, 1927, **46**, 105; **A.**, 400.

<sup>35</sup> *Bull. Soc. chim.*, 1927, **41**, 304; **A.**, 400.

individual lattices differ considerably in size. For example, T. Barth and G. Lunde<sup>36</sup> were able to prepare series of mixed crystals from halogen compounds of certain heavy metals (large lattices) with those of alkali metals (smaller lattices).

(b) In such cases, in general, the resulting lattice varies in a simple manner with the relative proportion of the constituents. Thus, L. Vegard,<sup>37</sup> in the case of mercurous chloride and bromide, found a linear increase in the lattice constants as the molecular content of the bromide increased from 0 to 100%. He also found that the rate of precipitation affected the size of the resulting lattice, the linear law holding for slow rates.

(c) Mixed crystals may be formed from constituents whose lattices differ in character. Thus, T. Barth and G. Lunde<sup>38</sup> found that thallous bromide (body-centred cubic) and thallous iodide (rhombic) form mixed crystals the lattice of which may be cubic or rhombic according to the proportion of the constituents, both types existing in the middle of the series. One crystal thus appears to be able to accommodate itself to the structure of the other crystal to some extent. This power of accommodation, however, is not necessarily equally shared by the two constituents. Thus in mixed crystals of silver bromide (cubic rock-salt type;  $a = 5.76 \text{ \AA.}$ ) and silver iodide (cubic zinc-blende type;  $a = 6.49 \text{ \AA.}$ ) both types may occur, but the bromide is able to include in its structure a large percentage of the iodide, although the converse is not true.

(d) In cases where the constituents are coloured, the mixed crystals often show a deeper colour than either constituent. Thus Barth and Lunde (*loc. cit.*) found this to be true for CuI-AgI and AgBr-AgI. They regard the coloration as due to distortion of the ions in fitting into the new lattice.

(e) L. Vegard and T. Hauge<sup>39</sup> find evidence by X-rays of the formation of mixed crystals when potassium bromide and chloride or when mercurous bromide and chloride in the solid phase are placed in contact. They suggest that an exchange of atoms between the crystal lattices occurs.

*Silicates.*—Reference was made in last year's report to the special rôle played by the oxygen atoms, owing to their predominant size and number, in many of the complex silicates. A general discussion of this subject with examples from recent new work is given in a paper by W. L. Bragg and J. West.<sup>40</sup> The following examples may be mentioned.

<sup>36</sup> *Z. physikal. Chem.*, 1926, **122**, 293; **A.**, 1926, 895.

<sup>37</sup> *Z. Physik*, 1927, **43**, 299; **A.**, 815.

<sup>38</sup> *Norsk Geol. Tidsskrift*, 1926, **8**, 293.    <sup>39</sup> *Z. Physik*, 1927, **42**, 1; **A.**, 504.

<sup>40</sup> *Proc. Roy. Soc.*, 1927, [A], **114**, 450; **A.**, 501; *Proc. Roy. Inst.*, 1927, **25**, 302.

*Cyanite* (one of the forms of  $\text{Al}_2\text{SiO}_5$ ). The crystal is triclinic, the unit cell, containing four molecules, being defined by  $a = 7.15$ ,  $b = 8.00$ ,  $c = 5.55 \text{ \AA.}$ ,  $\alpha = 90^\circ 5\frac{1}{2}'$ ,  $\beta = 101^\circ 2'$ ,  $\gamma = 105^\circ 44\frac{1}{2}'$ . In spite of the irregular character of this cell, it was found possible to fit it into a scheme of oxygen atoms (diameter  $2.70 \text{ \AA.}$ ) arranged in *cubic* close packing, an arrangement which was verified by an X-ray examination of the crystal. The low symmetry of the structure is thus due to the complexity introduced by the distribution of aluminium and silicon atoms amongst the interstices in the oxygen arrangement. Although this distribution is not determined, it is anticipated by analogy with other silicates that the aluminium and silicon atoms are respectively surrounded by groups of six and four oxygen atoms.

*The chondrodite series* <sup>41</sup> [*Chondrodite*,  $\text{Mg}(\text{OH})_2, 2\text{Mg}_2\text{SiO}_4$ , monoclinic; *humite*,  $\text{Mg}(\text{OH})_2, 3\text{Mg}_2\text{SiO}_4$ , orthorhombic; *clinohumite*,  $\text{Mg}(\text{OH})_2, 4\text{Mg}_2\text{SiO}_4$ , monoclinic]. The members of this series bear a strong crystallographic resemblance to olivine ( $\text{Mg}_2\text{SiO}_4$ ) and, with it, afford an interesting example of morphotropy; for, whilst two edges of the unit cell remain practically constant throughout the series, the thickness measured perpendicular to these edges varies in definite steps which are simply related to each other. The three structures may be described as being formed of alternate layers—parallel to the  $c$  face—of  $\text{Mg}(\text{OH})_2$  and  $\text{Mg}_2\text{SiO}_4$ , based on an arrangement of oxygen atoms and hydroxyl groups in *hexagonal* close packing. In this case, as in that of cyanite, the oxygen atoms appear to determine the dimensional relations, whilst the metal and silicon atoms control the symmetry in the unit cell. The layers of  $\text{Mg}_2\text{SiO}_4$  are found to possess the olivine structure.

*Phenacite* ( $\text{Be}_2\text{SiO}_4$ ).<sup>42</sup> The unit cell, which is rhombohedral and contains six molecules, has an angle of  $108^\circ 1'$  and a side of length  $7.68 \text{ \AA.}$  The arrangement of oxygen atoms differs somewhat from that in the preceding example in being more open. The trigonal axes in the structure are contained within narrow channels devoid of atoms, although elsewhere there is close packing. The structure may be regarded as built up of slightly staggered rows of oxygen atoms in contact parallel to the trigonal axes. These parallel rows may be divided into groups of four, arranged to form a new column of Y-shaped section. The Y-shaped columns are then packed together so that one column relative to its neighbours is displaced parallel to its length (and therefore to the trigonal axes) by an amount equal to the radius of an oxygen atom ( $1.35 \text{ \AA.}$ ). The silicon atoms, and probably also the beryllium atoms, lie within groups of four oxygen atoms.

<sup>41</sup> W. H. Taylor and J. West, *Proc. Roy. Soc.*, 1928, [A], 117, 517.

<sup>42</sup> W. L. Bragg, *ibid.*, 1927, [A], 113, 642; A., 97.

A recent determination<sup>43</sup> of the space groups of the members of the diopside group—diopside, phenacite, willemite, and troostite—shows that all four crystals have the symmetry of  $C_{2v}^2$ . The similarity in the X-ray diffraction patterns suggests that the phenacite structure is common to the series.

An interesting paper by R. W. G. Wyckoff and G. W. Morey<sup>44</sup> describes an X-ray investigation of compounds in the system soda-lime-silica. Of the four silicates of sodium and calcium, two—the orthosilicate,  $\text{Na}_2\text{CaSiO}_4$ , and metasilicate,  $\text{Na}_4\text{Ca}(\text{SiO}_3)_3$ —are optically isotropic, the third,  $\text{Na}_2\text{Ca}_2(\text{SiO}_3)_3$ , is slightly doubly refractive, whilst the fourth,  $\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$ , differs from the others crystallographically and optically. The X-ray diffraction patterns of the first three, and especially of the first two, show a strong similarity, although the third is definitely not cubic, the second probably only pseudo-cubic, and all three differ widely in chemical composition. Advantage was taken of the high symmetry to examine the structures of the ortho- and meta-silicates. Although that of the latter is not certain, it is considered probable that the silicon atoms are surrounded by four oxygen atoms. The unit cell of the orthosilicate is cubic, of side 7.50 Å., and contains four molecules. The oxygen atoms are arranged in groups of four about each silicon atom. The structure may be regarded as a distortion of a composite lattice of the NaCl and  $\text{CaF}_2$  type (see Fig. 1) in which the Ca and  $\text{SiO}_4$  groups are arranged as Na and Cl in rock-salt, and the Na and  $\text{SiO}_4$  groups as F and Ca atoms in fluorspar. The authors direct attention to the frequency of this structure for ionic compounds consisting of four groups. From a consideration of such compounds as  $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ ,  $(\text{NH}_4)_3\text{AlF}_6$ , and  $\text{Na}_2\text{CaSiO}_4$ , they conclude that “there is no obvious connection between the crystal structure of a crystal and the valency of its atoms.”

A further attempt to classify the micas<sup>45</sup> illustrates the difficulty of assigning to the more complex silicates formulæ having chemical significance. In the present case, the micas are regarded as “salts of an acid with a constant number (six) of silicon atoms.” This classification is based on the observation that the ratio  $\text{R}_2\text{O} : \text{SiO}_2 = 1 : 6$  is constant throughout the series.

*Isomorphous Substitution.*—The substitution of one set of atoms or group of atoms for another in a series of compounds, is not only of use in giving information of chemical value, but in the case of isomorphous series of complex solid compounds it can be a

<sup>43</sup> G. Gottfried, *Neue Jahrb. Min.*, 1927, [A], 55, 393.

<sup>44</sup> *Amer. J. Sci.*, 1926, 12, [v], 419; A., 1927, 10.

<sup>45</sup> A. F. Hallimond, *Min. Mag.*, 1925, 20, 305; A., 1925, ii, 819; 1926, 21, 25, 195; A., 1926, 815.



useful aid to the determination of the crystal structure by X-rays. The investigation of the alums quoted above is an example. A further example is that of the *alkali sulphates* of type  $R_2SO_4$ .<sup>46</sup> The sulphates of K, Tl,  $(NH_4)$ , and Cs were examined. The small scattering power for X-rays of the  $(NH_4)$  group permitted the more definite location of the sulphur atoms, whilst the relatively large scattering power of the caesium atom aided the location of the R atoms. The structure, as in other sulphates investigated, contains  $(SO_4)$  groups; each R atom is surrounded by six oxygen atoms. The unit cell is orthorhombic, contains four molecules, and possesses the symmetry of  $V_h^{16}$ . The atomic arrangement deduced explains the pseudo-hexagonal character of these sulphates.

Another isomorphous series recently examined is that of the tetragonal scheelite group.<sup>47</sup> The structures of  $BaWO_4$ ,  $PbWO_4$ ,  $BaMoO_4$ , and  $PbMoO_4$  are found to be identical with that of scheelite ( $CaWO_4$ ), in which the metal atoms may be regarded as arranged in a diamond type of lattice expanded in the direction of the *c* axis, the tungsten atoms being surrounded by four oxygen atoms. The replacement of calcium by barium or lead causes a considerable expansion of the scheelite lattice, the effect being greater for lead.

The series xenotime ( $YPO_4$ ), zircon ( $ZrSiO_4$ ), rutile ( $TiO_2$ ), and cassiterite ( $SnO_2$ )<sup>48</sup> is interesting as an example of a case where morphological isotropy is not necessarily accompanied by structural similarity. The similar structures of the first two crystals are found to differ from the similar structures of the second two.

*Colour and Crystal Structure.*—O. R. Howell<sup>49</sup> points out that it is in some cases possible to predict the structure of a crystal from its colour. It has been shown<sup>50</sup> that, when a metallic atom in a colourless insoluble compound is replaced by cobalt, a pigment is obtained which is blue if the cobalt is surrounded by four other atoms, and red if it is surrounded by six. From the colour of pigments, prepared in this way from compounds of unknown crystal structures, it was possible to predict in some measure the structure of the compound from which it was derived. For example, a blue compound is obtained when cobalt replaces zinc in zinc orthosilicate, whereas from magnesium orthosilicate a red pigment is obtained. The structures of both these silicates have now been determined:

<sup>46</sup> W. Taylor, *Proc. Manchester Lit. Phil. Soc.*, 1927 (in the press); A. Ogg, *Phil. Mag.*, 1928, 5, 354.

<sup>47</sup> L. Vegard and A. Refsum, *Skrifter Norske Videnskaps-Akad.*, 1927, 1, No. 2.

<sup>48</sup> L. Vegard, *ibid.*, No. 6.

<sup>49</sup> *J.*, 1927, 2843.

<sup>50</sup> R. Hill and O. R. Howell, *Phil. Mag.*, 1924, 48, 833; *A.*, 1924, ii, 817.

W. Zachariasen<sup>51</sup> finds zinc orthosilicate to be isomorphous with phenacite,  $\text{Be}_2\text{SiO}_4$ , in which the beryllium atom is between four oxygen atoms,<sup>42</sup> whereas the work of W. L. Bragg and G. B. Brown<sup>52</sup> on olivine has shown that in  $\text{Mg}_2\text{SiO}_4$  each magnesium atom is surrounded by six oxygen atoms. Other examples are given in Howell's paper.

*Crystal Structure of Boron Nitride.*<sup>53</sup>—Prepared crystals of BN were found to show a similarity in form and structure to graphite and not to diamond as was previously expected.<sup>54</sup> Each nitrogen atom is surrounded by three equidistant boron atoms and *vice versa*.

*Solid Oxygen.*<sup>55</sup>—X-Ray examination at  $-252^\circ$  reveals a body-centred orthorhombic cell of dimensions  $a = 5.50$ ,  $b = 3.82$ ,  $c = 3.44$  Å., containing two molecules. This is considered to be the lower-temperature modification.

#### *Theoretical Determinations of Crystal Parameters.*<sup>56</sup>

J. E. Lennard-Jones and (Miss) B. M. Dent have extended their work on the determination of crystal parameters from the inter-atomic forces, of which an account was given in last year's report, to other crystals with one parameter—the rutile group, chlorostannate and chloroplatinate of potassium, and solid carbon dioxide. Their results for the last are of interest, since they show a distance of  $0.90$  Å. between carbon and oxygen; this is in fair agreement with the value obtained by X-ray analysis by J. de Smedt and W. H. M. Keesom,<sup>57</sup> *viz.*,  $1.05$  Å., but appears to negative the results of H. Mark and E. Pohland,<sup>58</sup> who obtained  $1.59$  Å.

#### *Organic Crystals.*

The investigation of the detailed structure of organic crystals is peculiarly difficult. They are in general of relatively low crystallographic symmetry, the molecules are complicated, and a complete determination involves the fixing of a large number of parameters. This can only be done by measuring the intensities of the X-ray spectra, and for organic crystals such measurements are usually not easy to make (suitable specimens being difficult to obtain), and extremely difficult to interpret. Most of the investigations of

<sup>51</sup> *Norsk Geol. Tidsskrift.*, 1926, **9**, 65.

<sup>52</sup> *Z. Krist.*, 1926, **63**, 538; *A.*, 1926, 995.

<sup>53</sup> V. M. Goldschmidt and O. Hassel, *Sær. Norsk Geol. Tids.*, 1926, 258.

<sup>54</sup> H. G. Grimm and A. Sommerfeld, *Z. Physik*, 1926, **36**, 36; *A.*, 1926, 560.

<sup>55</sup> J. C. McLennan and J. O. Wilhelm, *Phil. Mag.*, 1927, [vii], **3**, 383; *A.*, 297.

<sup>56</sup> *Phil. Mag.*, 1927, [vii], **3**, 1204; *A.*, 715.

<sup>57</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1924, **27**, 839; *A.*, 1925, ii, 484.

<sup>58</sup> *Z. Krist.*, 1925, **61**, 293.

the structures of organic crystals have not attempted to go beyond the space group.

Space-group determinations may give useful information concerning the symmetry of the organic molecules. Of interest in this respect is recent work on the structure of a number of methane derivatives. On theoretical grounds a pyramidal structure, having the carbon atom at the vertex and the hydrogen atoms all in one plane, has been assigned to the methane molecule itself.<sup>59</sup> Work on the crystal structure of pentaerythritol,  $C(CH_2OH)_4$ , appeared to be in agreement with this; the arrangement of the groups around the single carbon atom was stated to be pyramidal,<sup>60</sup> and work on the external symmetry of the crystals<sup>61</sup> was supposed to confirm this. Quite recently I. Nitta<sup>62</sup> and S. B. Hendricks<sup>63</sup> have published work in which they show that the space group of the crystal is  $C_4^2$  and that the molecule may have a fourfold alternating axis of symmetry. This makes a tetrahedral molecule with the carbon atom in the centre a possibility. Support to this view is given by some work of A. Schleede and E. Schneider<sup>64</sup> who conclude from the growth of single crystals of pentaerythritol that the symmetry is  $S_4$  or tetragonal alternating. The balance of evidence at present appears to be in favour of a tetrahedral carbon atom in this compound.

In tetranitromethane H. Mark and W. Noethling<sup>65</sup> find that the molecule has a threefold axis. The carbon atom is thus tetrahedral, but only three of the nitro-groups are equivalent. The symmetry corresponds to the structural formula  $O \cdot NO \cdot C(NO_2)_3$ . In tetramethylmethane they find a tetrahedral group. W. H. George<sup>66</sup> has studied the isomorphism of the series carbon, silicon, germanium, and lead tetraphenyl. The crystals are tetragonal, and the unit cell, which contains two molecules, has an alternating fourfold axis of symmetry, parallel to the *c*-axis. The size of the square base of the cell increases and the height decreases with increasing atomic number of the quadrivalent element. The phenyl groups are in all cases arranged tetrahedrally about the central atom.

<sup>59</sup> V. Guillemin, jun., *Ann. Physik*, 1926, **81**, 173; *A.*, 1926, 1083.

<sup>60</sup> H. Mark and K. Weissenberg, *Z. Physik*, 1923, **17**, 301; *A.*, 1923, **i**, 1055; M. L. Huggins and S. B. Hendricks, *J. Amer. Chem. Soc.*, 1926, **48**, 164; *A.*, 1926, 227.

<sup>61</sup> H. G. K. Westenbrink and F. A. van Melle, *Z. Krist.*, 1926, **64**, 548; A. Giebe and E. Scheibe, *Z. Physik*, 1925, **33**, 346.

<sup>62</sup> *Bull. Chem. Soc. Japan*, 1926, **1**, 62; *A.*, 1926, 665.

<sup>63</sup> *Z. Krist.*, 1927, **66**, 131.

<sup>64</sup> *Naturwiss.*, Dec. 2nd, 1927.

<sup>65</sup> *Z. Krist.*, 1927, **65**, 435.

<sup>66</sup> *Proc. Roy. Soc.*, 1927, [A], **113**, 585.

*Long-chain Compounds.*—A notable advance has been made by A. Müller <sup>67</sup> in the study of the structure of the long-chain compounds. He has succeeded in obtaining rotation X-ray photographs and Laue photographs from small single crystals of stearic, bromostearic, stearolic, and behenolic acids. All the crystals are monoclinic-prismatic. Chains of carbon atoms exist in all four crystals. The chains are packed in the crystal with their axes parallel to one another or nearly so, the distance between carbon atoms in the chains being much less than the distance between neighbouring chains. The crystal molecule appears in all cases to be a chain of carbon atoms, the number of atoms in the chain being the same as that in the chemical molecule. It will readily be seen that an arrangement of this kind will give parallel sheets of carbon atoms very closely and evenly spaced within the unit cell. The true unit spacing perpendicular to the sheets will be large, but it will be very nearly exactly divided by the sheets of carbon atoms into a much smaller spacing. Suppose, for example, that the chain consisted of 19 exactly similar carbon atoms followed by a carbon atom united with a different group A, and that this was repeated indefinitely. The true spacing would be from an atom A to the next atom A, and there would be a large number of orders of spectra on the rotation photograph corresponding to this very long spacing. Had all the carbon atoms been alike, only the 20th, 40th, 60th of these spectra would have appeared. Actually the atoms are not all alike, and the intervening spectra do occur, but only those near the 20th, 40th, 60th spectra are at all strong, since it is only for these spectra that the contributions from all the carbon atoms are nearly in phase. Thus, by studying the periodic waxing and waning of the intensities of a large series of spectra, valuable information as to the arrangement of the carbon atoms can be obtained, even although exact measurements of intensity cannot be made.

It is interesting to note that the molecular cross-section parallel to the basal plane of the crystal, as determined by Müller, agrees very closely with Adam's estimate of the cross-section in his work on unimolecular surface films.

In conclusion the authors wish to express their indebtedness to Prof. W. L. Bragg, F.R.S., for many helpful suggestions during the preparation of this Report.

R. W. JAMES.

J. WEST.

A. J. BRADLEY.

<sup>67</sup> *Proc. Roy. Soc.*, 1927, [A], 114, 542.

## MINERALOGICAL CHEMISTRY.

GROTH is dead. Paul Heinrich Ritter von Groth (1843—1927) died on December 2nd at the ripe age of 84½ years. He was Professor of Mineralogy in Strassburg during 1872—1883, and since 1883 in Munich, and his laboratory was long the centre of training for students from all parts of the world. In 1877 he founded the *Zeitschrift für Krystallographie und Mineralogie* (carried on since 1921 by Prof. Paul Niggli of Zürich under the title *Zeitschrift für Kristallographie*), in which he obtained the willing co-operation of workers in all countries. As marking the jubilee of that periodical, he gave in vol. 66, only shortly before his death, an interesting review of the work that had been done. His monumental work, "Chemische Krystallographie" (5 vols., 1906—1919), collects together the crystallographic data for some 7350 substances. The extent to which this is now being used by X-ray workers could scarcely have been foreseen even by Groth himself. His well-known text-books "Physikalische Krystallographie" and "Tabellarische Übersicht der Mineralien" each passed through four editions, and only last year he gave an interesting essay on the historical development of the mineralogical sciences.<sup>1</sup> He held a unique position as a leader, and he did more than anyone else in co-ordinating and stabilising crystallographic nomenclature and methods. His name will for ever stand out as a landmark in the history of crystallography.

The deaths<sup>2</sup> have also to be recorded of two distinguished mineral chemists, who both did valuable work, but on entirely different lines. William Francis Hillebrand (1853—1925), as chemist on the United States Geological Survey, had made many analyses of minerals and rocks, including several rare and new minerals collected by members of the survey in new country. The careful and detailed analytical work for which he was noted led to the recognition of several chemical elements not previously suspected to be present in rocks. In 1888—1892 he made a number of very detailed analyses of uraninite (pitchblende), in which he found a gas. This

<sup>1</sup> "Entwicklungsgeschichte der mineralogischen Wissenschaften," Berlin, 1926.

<sup>2</sup> L. J. Spencer, "Biographical Notices of Mineralogists Recently Deceased" (third series), *Min. Mag.*, 1927, 21, 229.

gas evidently puzzled him, and he concluded that it was mainly nitrogen. Sir William Ramsay afterwards, in 1895, identified it as helium, and uraninite was the first known terrestrial source of this element. Hillebrand's well-known book "Analysis of Silicate and Carbonate Rocks" was first issued in 1907 as a Bulletin of the United States Geological Survey, and has passed through several editions. Working as a student in Heidelberg under Bunsen he prepared metallic cerium in 1875 and discovered its pyrophoric property, a property which now has an extensive practical application.

Gustav von Tschermak (1836—1927), of Vienna, died on May 4th, at the advanced age of ninety-one years. As distinct from the work of Hillebrand, his work consisted largely in correlating the large amount of data accumulated by analytical chemists and in deducing general principles. The current views of the text-books on the constitution of many of the main groups of silicates are due to him, and were developed in a series of classical papers extending over many years: plagioclase feldspars (1865), pyroxenes and amphiboles (1868), micas (1877), scapolites (1884), chlorites (1890), vermiculites (1891), tourmaline (1899), zeolites (1917—1918). In later years, with the help of his pupils (including his daughter Silvia Hillebrand), he endeavoured to determine the composition of silicic acids isolated from natural silicates. The valuable periodical *Tschermaks Mineralogische und Petrographische Mitteilungen* was commenced by him in 1872, and his well-illustrated "Lehrbuch der Mineralogie" passed through nine editions.

Mineralogical jubilees are now falling due. That of the Mineralogical Society of Great Britain and Ireland (instituted February 3rd, 1876) was celebrated last year,<sup>3</sup> and was attended by several distinguished foreign mineralogists. The Société française de Minéralogie was founded on March 21st, 1878, and the fifty volumes of its Bulletin show a record of brilliant work. As noted above, Groth's *Zeitschrift* and Tschermak's *Mitteilungen* were commenced in 1877 and 1872 respectively. The Russian Mineralogical Society dates from a much earlier period (1817), whilst those of Vienna (1901), Germany (1908), America (1919), and Switzerland (1924) are later.

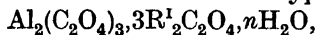
<sup>3</sup> Account of the jubilee celebration, *Min. Mag.*, 1926, 21, 99-148. Reference is there made to the earlier British Mineralogical Society (1799-1806), which consisted of a small group of chemists, including Arthur Aikin, who offered to "examine, free of expense, all specimens of earths or soils, with a view to determining the nature and proportions of their different contents." That society led to the foundation of the Geological Society of London in 1807.

*Geochemical Distribution of the Elements.*

The series of elaborate papers under this title has been continued by V. M. Goldschmidt,<sup>4</sup> but in the later numbers the scope of the investigation has been gradually changing—dealing with X-ray determinations of the crystal structure of the rare-earth oxides, the laws of crystal chemistry, etc. It is suggested that elements showing some homœomorphous relation between the crystal structure of their compounds should be found in association in nature. However, work on the original lines has been continued by some of his collaborators. G. Lunde<sup>5</sup> has examined a variety of minerals and basic igneous rocks from Norwegian localities for traces of platinum metals, finding 0.0000074% Pt in an olivine-rock and in hornblende-gabbro, and 0.000006% in tantalite. The wide distribution of traces of iodine has been further investigated by T. von Fellenberg and G. Lunde.<sup>6</sup> In meteoric irons and stones, amounts of iodine up to 0.000018% have been detected, together with up to 0.00056% of bromine, the latter especially in the stones. Systematic search for such elements, which are widely distributed although never found in concentrated quantities, is, of course, of some economic importance.

*Constitution of Silicates.*

A comparative study of mineral silicates with the more tractable organic silicon compounds would no doubt throw some light on the constitution of the former. Some comparisons of this kind were made by the late J. Emerson Reynolds, and by the oxidation of the compound  $\text{CaSi}_2\text{Al}_2$  (analogous to  $\text{CaC}_2\text{N}_2$ ) he synthesised anorthite by an interesting method. A long series of valuable papers by F. S. Kipping and his co-workers on organic derivatives of silicon has appeared in the *Journal* of this Society since 1901. G. N. Ridley,<sup>7</sup> in a brief outline of some of the present views on the constitution of the silicates, has compared ethyl orthosilicate,  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , with olivine,  $\text{Mg}_2\text{SiO}_4$ , and ethyl metasilicate,  $\text{SiO}(\text{OC}_2\text{H}_5)_2$ , with enstatite,  $\text{MgSiO}_3$ . On similar lines, W. Wahl has compared aluminosilicates with alumino-oxalates, tracing, it would appear, a close analogy. He had recently proved<sup>8</sup> that certain alkali aluminium trioxalates of the type



<sup>4</sup> "Geochemische Verteilungsgesetze der Elemente," Nos. I–VIII, *Videnskapsel. Skrifter, Kristiania* (later *Skrifter Norske Videnskaps-Akad. Oslo*), 1923–7; compare *Ann. Report*, 1923, 20, 262.

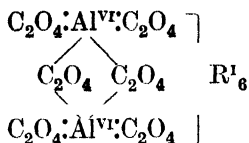
<sup>5</sup> *Z. anorg. Chem.*, 1927, 161, 1; *A.*, 439.

<sup>6</sup> *Biochem. Z.*, 1926, 175, 162; *A.*, 1926, 1022; 1927, 187, 1; *Beitr. Geophysik*, 1927, 16, 413.

<sup>7</sup> *Chem. News*, 1925, 131, 305; *A.*, 1925, ii, 1130.

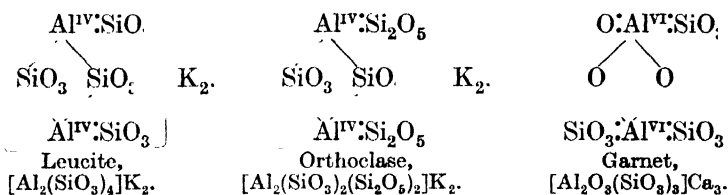
<sup>8</sup> *Ber.*, 1927, 60, [B], 399; *A.*, 339.

usually regarded as "double salts," can be split up into optically active enantiomorphous isomerides. It therefore becomes necessary



to write a co-ordination formula with a central sexavalent ("co-ordination number" 6) aluminium atom, the six  $\text{C}_2\text{O}_4$  groups being arranged as at the corners of an octahedron to form the tervalent anion.

One of the nine possible types of aluminooxalates is here shown with two aluminium atoms. In some other cases a central quadrivalent aluminium atom forms with two  $\text{C}_2\text{O}_4$  groups a univalent anion, giving the complex  $[\text{C}_2\text{O}_4 \cdot \text{Al}^{\text{IV}} \cdot \text{C}_2\text{O}_4] \text{R}^1$ . The aluminosilicates are suggested<sup>9</sup> to be analogous to these aluminooxalates, and formulæ on the same lines are given for numerous minerals, a "silicyl" group,  $\text{SiO}_3$ , or a "bisilicyl" group,  $\text{Si}_2\text{O}_5$ , taking the place of the oxalato-group. Some of the formulæ, e.g., for the micas, are written to show the polymerisation of the molecule, and these are so large and complex that they are given as text-figures. The following examples may be quoted:



These formulæ suggest an explanation for the breaking down of orthoclase into leucite and silica at a high temperature, for the alteration of felspar to kaolin, of garnet to chlorite, etc. The aluminosilicates being all high-temperature compounds, such formulæ cannot be tested by the methods of stereochemistry, as in the case of organic compounds. They are essentially different from the co-ordination formulæ proposed by J. Jakob.<sup>9a</sup>

It is further suggested<sup>10</sup> that silicon is not always quadrivalent in the silicates. In the fluosilicates the silicon atom is surrounded by six fluorine atoms and the co-ordination formula is  $[\text{Si}^{\text{IV}}\text{F}_6] \text{R}_2^1$ . If the fluorine is replaced by oxygen, the compound  $[\text{Si}^{\text{IV}}\text{O}_6] \text{R}_2^1$ , with the same empirical composition as a metasilicate, is obtained. This is assigned to clinoenstatite, which at a high temperature breaks down into forsterite and silica. A compound similar to this, together with "syntagmatite" and an addition product of

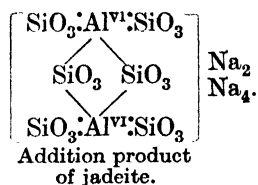
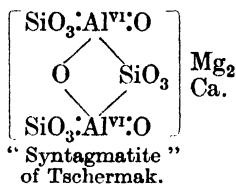
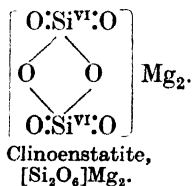
<sup>9</sup> W. Wahl, *Finska Kemistsamfundets Meddelanden*, 1927, Nos. 1 & 2, 40 pp.; *Z. Krist.*, 1927, **66**, 33, 173.

<sup>9a</sup> *Helv. Chim. Acta*, 1920, **3**, 669; *A.*, 1920, ii, 754; *Z. Krist.*, 1921 **56**, 295; see *Ann. Report*, 1923, **20**, 266.

<sup>10</sup> W. Wahl, *Ann. Acad. Sci. Fennicae*, Ser. A, 1927, **29**, No. 22.



jadeite, would give molecules with sufficient structural similarity to form isomorphous mixtures, and so explain the presence of aluminium in the amphiboles.



Here there is a replacement of silicon atoms with a co-ordination number of 6 by aluminium atoms also with a co-ordination number of 6. Such a replacement had indeed been suggested for the aluminous amphiboles by P. A. von Bonsdorff in 1821, but this was acceptable only before the current ideas of valency had developed, and these, it seems, must now be modified.

An interesting attempt to elucidate the constitution of the silicates has been made by W. L. Bragg,<sup>11</sup> who has attacked the problem from an entirely new point of view. From the results arrived at by the determination of crystal structures by *X*-ray methods, it is suggested that the structure of silicates is governed by the arrangement of the oxygen atoms. These are assumed to be the largest of all the atoms that enter into the composition of the silicates, and the diameter assigned to them is 2.7 Å. A symmetrical arrangement of such atoms, according to either the cubic or the hexagonal plan of closest packing, is supposed to form the foundation of most silicate structures. The smaller atoms of silicon and of the constituent metals merely fall into the interspaces between the oxygen atoms. In most cases it appears that the silicon atoms lie at the centre of a tetrahedral group of four oxygen atoms, as in the building unit assigned to β-quartz<sup>12</sup> and tridymite.<sup>13</sup> In determining the structure by *X*-ray methods of any particular mineral, an attempt is made to locate the precise position of each atom. The relative positions of the several atoms will then give some idea of the chemical constitution.

In 1920 W. L. Bragg,<sup>14</sup> in a series of calculated atomic diameters, gave that of oxygen (1.30 Å.) as the smallest of all the elements. To be told now that it is the largest of all is somewhat disconcerting. If oxygen is to play the governing part in the structure of the silicates,

<sup>11</sup> *Proc. Roy. Soc.*, 1927, [A], 114, 450; A., 501; *Proc. Roy. Inst.*, 1927, 25, 302.

<sup>12</sup> (Sir) W. H. Bragg and R. E. Gibbs, *Proc. Roy. Soc.*, 1925, [A], 109, 405; A., 1926, 13.

<sup>13</sup> R. E. Gibbs, *ibid.*, 1926, [A], 113, 351; A., 1927, 10.

<sup>14</sup> *Ann. Report*, 1920, 17, 201.

it should presumably also do so in the many other oxygen salts; and we might consequently argue that there would be only minor differences in structure between  $\text{CaSiO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CaSO}_3$ ,  $\text{NaNO}_3$ , and  $\text{NaClO}_3$ , or between  $\text{ZrSiO}_4$ ,  $\text{CaSO}_4$ ,  $\text{AlPO}_4$ ,  $\text{KClO}_4$ , etc. As a matter of fact, these are all very different, the only striking similarity being between  $\text{CaCO}_3$  and  $\text{NaNO}_3$ . Further, it is difficult to accustom ourselves to the idea that silicon is not an essential and really important constituent of the silicates. In many of their characters silicates are markedly different from other oxygen salts. They are, for example, usually distinguished by a high degree of hardness,<sup>15</sup> as compared with the relatively soft carbonates, sulphates, etc. The considerable difference in hardness (5 and 7 on Mohs's scale) in two directions on the same face of a crystal of kyanite presents a peculiar problem; and it must not be forgotten that talc is the softest of minerals.

V. M. Goldschmidt,<sup>16</sup> on the other hand, points out similarities in crystal structure between  $\text{Zn}_2\text{SiO}_4$  (willemite) and  $\text{Li}_2\text{BeF}_4$ , and between  $\text{CaMgSi}_2\text{O}_6$  (diopside) and  $\text{NaLiBe}_2\text{F}_6$ . These are evidently homœomorphous relations depending on nearness of molecular volume, as pointed out for many similar cases by J. D. Dana in 1850. In the same place V. M. Goldschmidt suggests that diopside is the calcium salt of "diopside" acid,  $\text{H}_2\text{MgSi}_2\text{O}_6$ , and jadeite the sodium salt of "jadeite" acid,  $\text{HAlSi}_2\text{O}_6$ . In another direction he argues,<sup>17</sup> from certain similarities in structure between  $\text{Mg}_2\text{SiO}_4$  (olivine) and  $\text{K}_2\text{SO}_4$  on the one hand and  $\text{Al}_2\text{BeO}_4$  (chrysoberyl) on the other, that the first is an orthosilicate. For the metasilicates  $\text{MgSiO}_3$  (enstatite) and  $\text{CaSiO}_3$  (wollastonite) he finds no other compounds  $\text{ABX}_3$  of the same crystal type, and it is suggested that  $\text{MgSiO}_3$  is not a metasilicate, but may be  $\text{Mg}_2\text{SiO}_4 + \text{SiO}_2$ , and that orthoclase,  $\text{KAlSi}_3\text{O}_8$ , may be  $\text{KAlSiO}_4 + 2\text{SiO}_2$ .

Crystallographic similarities, based on "comparative external morphology" as shown by the development of zones and crystal faces, are used as a basis of classification by P. Niggli in the second edition of his "*Lehrbuch der Mineralogie*" (vol. 2, 1926). Here we find silicates ranged with a variety of other minerals: e.g., phenacite with cuprite, wollastonite with borax, kaolin with graphite, tourmaline with aragonite, etc. When the imagination is given full play, crystallography appears to open out endless possibilities. By the skilful manipulation of axial ratios and neglecting discrepancies corresponding with angles up to  $7\frac{1}{2}^\circ$  (i.e., half the

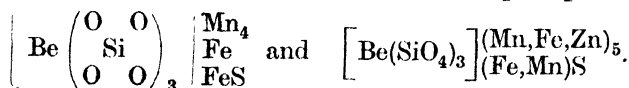
<sup>15</sup> The relation between hardness and crystal structure has been discussed by V. M. Goldschmidt, *Skrifter Norske Videnskaps-Akad.*, 1927 (for 1926), No. 8, p. 102.

<sup>16</sup> *Ibid.*, p. 131.

<sup>17</sup> *Ibid.*, 1926, No. 1, p. 110.

difference between  $30^\circ$  and  $45^\circ$ ), it is of course possible to demonstrate crystallographically any similarity that may be desired.<sup>18</sup>

Helvine, as dark brown tetrahedra associated with fluorite and garnet in pegmatite from a new occurrence in Argentina, has been analysed by W. Fischer,<sup>19</sup> who also gives a full discussion of the various formulæ that have been proposed for this and the closely allied mineral danalite. This analysis [ $\text{SiO}_2$ , 32.65;  $\text{BeO}$ , 12.20;  $\text{MnO}$ , 30.79;  $\text{FeO}$ , 14.75;  $\text{ZnO}$ , 4.89;  $\text{MgO}$ , 2.24;  $\text{S}$ , 6.01; total (less  $\text{O}$  for  $\text{S}$ ), 100.54], in showing the presence of some zinc, indicates a transition from helvine to danalite. When ignited in air the mineral gains 3.18% in weight, and water then extracts iron and manganese sulphates. The formula of helvine was formerly expressed as a double compound of the orthosilicate and monosulphide of the bivalent metals  $3(\text{Mn}, \text{Be}, \text{Fe})_2\text{SiO}_4, (\text{Mn}, \text{Be}, \text{Fe})\text{S}$ . Since, however,  $\text{Be} : (\text{Mn}, \text{Fe})$  is in the constant ratio 3 : 4, the formula is better written as  $3(\text{Mn}, \text{Fe})\text{BeSiO}_4, (\text{Mn}, \text{Fe})\text{S}$  or  $(\text{Mn}, \text{Fe})_4\text{Be}_3(\text{SiO}_4)_3\text{S}$ , representing an isomorphous mixture of  $3\text{MnBeSiO}_4, \text{MnS}$  and  $3\text{FeBeSiO}_4, \text{FeS}$ . This formula was written by Brögger and Bäckström (1890) in the form  $(\text{Mn}, \text{Fe})_2(\text{Mn}_2\text{S})^{\text{II}}\text{Be}_3(\text{SiO}_4)_3$  in order to show a relation to the garnet group  $\text{R}^{\text{II}}_3\text{R}^{\text{III}}_2(\text{SiO}_4)_3$ , where  $\text{Be}_3$  takes the place of  $\text{Al}_2$ , etc. J. Jakob (1920) gave a co-ordination formula, which was modified by W. Fischer, the two being, respectively,



But, as pointed out by V. M. Goldschmidt,<sup>20</sup> this formula corresponds with the ratios  $1\text{Be} : 6(\text{Mn}, \text{Fe}) : 3\text{Si} : 12\text{O} : 1\text{S}$ , whilst the analyses give  $\text{Be}_3(\text{Mn}, \text{Fe})_4\text{Si}_3\text{O}_{12}\text{S}$ . X-Ray powder photographs of helvine<sup>21</sup> are very similar to those given by sodalite, and the unit cubes of edges 8.19 and 8.85 Å. contain two molecules,  $\text{Be}_6\text{Mn}_8\text{Si}_6\text{O}_{24}\text{S}_2$  and  $\text{Al}_6\text{Na}_8\text{Si}_6\text{O}_{24}\text{Cl}_2$  (sodalite), respectively. C. Gottfried,<sup>22</sup> however, finds only one such molecule of helvine in a unit cell of edge 8.52 Å.

Another mineral belonging to the same group and also crystallising as regular tetrahedra is the zunyite from Zuñy mine, Colorado. A new analysis<sup>23</sup> agrees very closely with the earlier analyses of W. F. Hillebrand (1883) and S. L. Penfield (1893), from which the

<sup>18</sup> An example that has always acted personally as a warning in this direction is that given by the comparison of the axial ratios of andorite ( $\text{PbAgSb}_3\text{S}_8$ ), aeschynite, columbite ( $\text{FeNb}_2\text{O}_6$ ), and chalcostibite ( $\text{CuSbS}_2$ ) (see *Min. Mag.*, 1897, 11, 286; 1907, 14, 320).

<sup>19</sup> *Bol. Acad. Nac. Ciencias, Córdoba*, 1925, 28, 133; *Centr. Min.*, [A], 1926, 33.

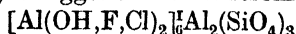
<sup>20</sup> *Centr. Min.*, [A], 1926, 148.

<sup>21</sup> T. Barth, *Norsk Geol. Tidsskr.*, 1926, 9, 40.

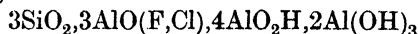
<sup>22</sup> *Z. Krist.*, 1927, 65, 425.

<sup>23</sup> B. Gossner and F. Mussnug, *Centr. Min.*, [A], 1926, 149.

empirical formula  $H_{18}Al_{16}Si_6(O,F,Cl)_{45}$  was deduced by Hillebrand. This was modified by Brögger and Bäckström as



to correspond with the garnet formula. B. Gossner and F. Mussgnug devised a formula,  $SiO_2, AlF(OH)_2, 2AlO_2H$  or  $2SiO_2, 2AlOF, 3AlO_2H$ , in which  $SiO_2$  is partly replaceable by  $AlO_2H$  or  $AlOF$  (as suggested by the homœomorphism of  $TiO_2$  and  $MgF_2$ ). Later,<sup>24</sup> however, on the ground of X-ray examination of the material analysed, the formula was adjusted so that six molecules



shall be contained in the unit cube of edge 13.92 Å. Surely this is only leading to greater complexity, if not confusion.

B. Gossner has also employed X-ray methods for the purpose of deducing the probable chemical formulæ of some other complex silicates, the formula being readjusted so as to give a whole number of molecules in the unit cell. For example, for the mineral leifite (of O. B. Bøggild, 1915), as calculated from the original formula  $Na_2Al_2Si_3O_{22}, 2NaF$  ( $M = 788.5$ ), the unit hexagonal cell of dimensions  $a = 14.34$ ,  $c = 4.93$  Å. would contain 1.78 molecules. Adoption of a formula  $Na_2Si_4O_9, AlOF$  ( $M = 359.5$ ) gives 3.83 molecules in the unit cell, and this is considered a sufficiently close approximation to 4 to justify the new formula.<sup>25</sup>

An exhaustive discussion on the chemical composition of the numerous minerals of the complex group of chlorites has been given by J. Oroel.<sup>26</sup> After a detailed historical review of the various theories of their constitution, he comes to the conclusion that before these theories can be thoroughly tested more data must be accumulated. He therefore gives a series of new analyses, with density and optical determinations, for nineteen chlorites belonging to various types, including two new types—an aluminous sheridanite and a magnesian thuringite. These and earlier analyses (290 in number) are calculated to the ratios  $SiO_2/R_2O_3$ ,  $FeO/MgO$ ,  $Fe_2O_3/Al_2O_3$ , and  $Cr_2O_3/Al_2O_3$ , and only empirical formulæ are given. On these ratios is based a new classification of the chlorites: I, Amesite, with  $SiO_2/R_2O_3 = s = 1$ . II, Corundophyllite group,  $s = 1.33$  to 1.66. III, Prochlorite group,  $s = 1.66$  to 2.33. IV, Prochlorite-clinochlore group,  $s = 2.33$  to 2.66. V, Clinochlore group,  $s = 2.66$  to 3.33. VI, Clinochlore-pennine group,  $s = 3.33$  to 3.5. VII, Pennine group,  $s = 3.5$  to 4.5. VIII, Chlorites poor in alumina,  $s > 4.5$ . Each of these groups is sub-divided according to the ratios  $FeO/MgO$  and  $Fe_2O_3/Al_2O_3$ ; but for the ratio  $Cr_2O_3/Al_2O_3$

<sup>24</sup> B. Gossner, *Jahrb. Min. Beil.-Bd.*, [A], 1926, 55, 319.

<sup>25</sup> B. Gossner and F. Mussgnug, *Centr. Min.*, [A], 1927, 221.

<sup>26</sup> *Bull. Soc. franç. Min.*, 1927, 50, 75; Thèse, Paris, 1927, 380 pp.; *A.*, 1923, ii, 647; 1924, ii, 621; 1925, ii, 821; *A.*, 1926, 42, 933, 1119.

the chromiferous chlorites are treated in the text as a special group, IX. To fit this classification certain chlorites (aphrosiderite, thuringite, bavalite, daphnite, delessite, diabantite, leuchtenbergite, kotschubeite) have been re-defined, whilst other terms (rumpfite, chloropite, protochlorite, dumasite, pseudophite) are regarded as superfluous. Optical data are tabulated with the chemical ratios given above, and it is shown that chlorites of different chemical composition may differ in some cases only slightly optically (*e.g.*, grochanites, clinochlores, and prochlorites). Also dehydration experiments (time-heating curves and pressure of aqueous vapour when the mineral was heated in a vacuum) led to no definite results. Chlorites are usually thought to be secondary minerals, but they may also occur as primary constituents of igneous rocks.

The work of H. S. Washington and H. E. Merwin on the chemical composition and optical and other data of the pyroxenes and amphiboles has been extended to the acmitic pyroxenes,<sup>27</sup> and valuable data, all determined on the same sample of material, are recorded. They find that the molecules acmite ( $\text{Ac} = \text{Na}_2\text{O}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$ ), jadeite ( $\text{Jd} = \text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ ), vanadous acmite ( $\text{Vac} = \text{Na}_2\text{O}, \text{V}_2\text{O}_3, 4\text{SiO}_2$ ), diopside ( $\text{Di} = \text{CaO}, \text{MgO}, 2\text{SiO}_2$ ), and hedenbergite ( $\text{Hd} = \text{CaO}, \text{FeO}, 2\text{SiO}_2$ ) may mix in all proportions. For example, an "acmitic diopsidic hedenbergite" is represented by the formula  $\text{Ac}_{10}\text{Jd}_6\text{Di}_{17}\text{Hd}_{60}\Delta_7$ , where  $\Delta$  represents the sum of such molecules as  $\text{FeO}, \text{SiO}_2$ ;  $\text{Fe}_2\text{O}_3, 3\text{SiO}_2$ ;  $\text{Al}_2\text{O}_3, 3\text{SiO}_2$ , etc. Excess of sesquioxides is assumed to be present as  $\text{R}_2\text{O}_3, 3\text{SiO}_2$ , rather than in the molecules  $\text{FeO}, \text{Fe}_2\text{O}_3, 4\text{SiO}_2$  and  $\text{FeO}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ , or in solid solution uncombined with silica. Arfvedsonite from Greenland has been the subject of detailed determinations by S. G. Gordon.<sup>28</sup> The analyses are interpreted as mixtures of the arfvedsonite molecule ( $\text{R}_2\text{O}, 3\text{RO}, 4\text{SiO}_2$ ), riebeckite molecule ( $\text{R}_2\text{O}, \text{R}_2\text{O}_3, 4\text{SiO}_2$ ), and usually an excess of  $\text{R}_2\text{O}_3$ , where  $\text{R}_2\text{O}$  is largely  $\text{Na}_2\text{O}$ , and  $\text{RO}$  and  $\text{R}_2\text{O}_3$  are chiefly  $\text{FeO}$  and  $\text{Fe}_2\text{O}_3$  respectively.

#### *Examination of Minerals by X-Ray Methods.*

The crystal structures of a large number of minerals have now been determined by X-ray methods, and a considerable mass of data has been accumulated and in part tabulated.<sup>29</sup> Unfortunately,

<sup>27</sup> *Amer. Min.*, 1927, **12**, 233.

<sup>28</sup> *Proc. Acad. Nat. Sci. Philadelphia*, 1927, **79**, 193.

<sup>29</sup> L. J. Spencer in "Tables annuelles de constantes et données numériques," vol. 5 (for 1917—22), p. 1391, Paris, 1926; vol. 6 (for 1923—4), p. 1226, Paris, 1928. R. W. G. Wyckoff in "International Critical Tables," vol. 1, p. 338, Washington, 1926. And in greater detail by P. P. Ewald and C. Hermann, "Strukturbericht, 1913—26," issued as separately-paged supplements in *Z. Krist.*, 1927, **65** et seq.

however, these data have only rarely been correlated with constants determined by other methods on the same sample of material. The majority of original papers give very little idea as to the kind of material that has been used in the experiments, and sometimes it is not clear whether artificially prepared material or a natural mineral has been employed. Due attention does not seem to have been always paid to the careful selection of material, and in a few cases even the identity of the mineral appears to be open to doubt.

Most X-ray workers are content to quote the crystallographic data and density, and even the chemical composition of the material in hand, from P. Groth's "Chemische Krystallographie" (5 vols., 1906—1919). This is a most useful standard work of reference for the crystallographic constants of artificially prepared chemical compounds; but for minerals it is admittedly incomplete, with only a few of the more important references to the original literature, the idea being that the full information was already available in the text-books on mineralogy. For example, under the heading "Beryllialuminiummetasilicat =  $\text{Si}_6\text{O}_{18}\text{Al}_2\text{Be}_3$ ," Groth gives a very inadequate account of the mineral species beryl. There are several varieties of this mineral. Some contain up to 5% of alkalis (usually cæsium) and most contain up to 2% of water. The text-book formula of beryl can be regarded as only approximate, and it may be doubted if the mineral is really a metasilicate. The density of beryl is given by Groth as 2.6—2.7, but recent determinations show a range from 2.545 to 2.910. The hexagonal crystals, although well developed, sometimes show optical anomalies and a complex intergrowth in sectors. Now, based on this information taken from Groth, a most elaborate structure has been built up for beryl as deduced from the examination of a crystal (or crystals?) by X-ray methods.<sup>30</sup> Not the slightest indication is given in the original paper of the kind of material used for this investigation; there is no mention of colour (a useful guide to the varieties of beryl), density, or other characters. "The X-ray measurements lead to a value 2.661 for the density"—but a direct determination would have been more useful.

The same authors<sup>31</sup> have also, on data quoted from Groth, deduced structures to explain the morphotropic relations of the humite group of minerals. This group has frequently been quoted as a classical example of a morphotropic series. These morphotropic relations are based on the chemical formulæ of Penfield and Howe (1894), which have never been confirmed; and recently they

<sup>30</sup> W. L. Bragg and J. West, *Proc. Roy. Soc.*, 1926, [A], 111, 691; *A.*, 1926, 889.

<sup>31</sup> *Idem, ibid.*, 1927, [A], 114, 450; *A.*, 501.

have been called into question by G. Cesàro,<sup>32</sup> who has deduced other formulæ from the original analyses. Further, H. Sjögren's "prolectite" (1895), supposed to be an end member of this series, has been proved to have no existence.<sup>33</sup> The three minerals chondrodite, humite, and clinohumite are not easy of determination and distinction, and it would not appear that the X-ray method affords a practical test.

It is evident that in the examination of minerals exclusively by a single method, such as the X-ray method, a too narrow view is being taken. The same undue importance is often also attached to optical methods in mineralogy. The only papers on minerals in which the materials have been completely examined by all available methods, including X-ray methods, are those by G. Aminoff. For the minerals bromellite,<sup>34</sup> magnetoplumbite,<sup>35</sup> swedenborgite,<sup>36</sup> and trimerite,<sup>37</sup> the crystallographic constants, crystal structure, optical data, density, chemical composition, etc., have all been determined on the same sample of material. The history, origin, and paragenesis of the minerals are concisely stated, and the main facts and data are clearly set out, for the benefit of the reader or recorder, without being confused with a mass of more or less irrelevant speculation. Further, the papers are presented once for all in a completed and finished form. There are no preliminary notices, reprints with minor modifications and corrections, and translations in other journals. This simplifies the literature and the work of the bibliographer. These excellent papers may well be taken as a pattern.

Several minerals of the pyroxene group have been examined and compared by the X-ray powder method;<sup>38</sup> and here in several cases the work was done on material that had been previously completely determined chemically and optically by the same authors. These minerals give patterns of four main types: (1) Diopside (including hedenbergite, acmite, jadeite, augite); (2) Enstatite (and hypersthene); (3) Wollastonite (and bustamite, pectolite, schizolite); (4) Rhodonite (and calcium-rich rhodonite). Some others (clinoenstatite, spodumene, alamosite, pyroxmangite, sobralite, babingtonite) give other types of pattern. It was found that the replacement of MgO by FeO produces practically no change

<sup>32</sup> *Bull. Acad. roy. Belg.*, 1926, **12**, 350; *A.*, 1927, 336.

<sup>33</sup> P. Geijer, *Geol. För. Förh.*, 1926, **48**, 86.

<sup>34</sup> *Z. Krist.*, 1925, **62**, 113; *Ann. Report*, 1925, **22**, 277.

<sup>35</sup> *Geol. För. Förh.*, 1925, **47**, 283.

<sup>36</sup> *Ibid.*, 1926, **48**, 19.

<sup>37</sup> *Z. Krist.*, 1924, **60**, 262; *Ann. Report*, 1925, **22**, 279.

<sup>38</sup> R. W. G. Wyckoff, H. E. Merwin, and H. S. Washington, *Amer. J. Sci.*, 1925 [v], **10**, 383; *A.*, 1925, ii, 1126.

in the structure; MnO has a slightly greater volume, and CaO an appreciably greater volume. In augite the excess of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  has no appreciable effect.

The unit-cell dimensions of the isomorphous members of the garnet group have been determined by G. Menzer<sup>39</sup> and also by C. H. Stockwell.<sup>40</sup> The latter has determined for 40 garnets the refractive index, specific gravity, and the edge of the unit cube (by the X-ray powder method). In only two cases, however, were the determinations made on analysed material; but with the aid of the previous work of W. E. Ford (1915) on the refractive index and specific gravity of the garnets, a correlation was obtained with the chemical composition. Plotting refractive index against specific gravity, Ford found that the garnets fall into two series (almandine-pyrope-spessartine and grossular-andradite), and this is emphasised by plots of the cell dimensions against either the refractive index or the specific gravity. From these data (with, in some few cases, a supplementary qualitative test for manganese), Stockwell was able to determine the nature of a given garnet, and the percentage molecular composition can be calculated. The calculated values for the pure molecules are :

	<i>n.</i>	<i>d.</i>	<i>a.</i>
Pyrope, $\text{Mg}_3\text{Al}_2(\text{SiO}_4)_3$ .....	1.705	3.510	11.430 Å.
Almandine $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$ .....	1.830	4.250	11.493
Spessartine, $\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$ .....	1.800	4.180	11.568
Grossular, $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ .....	1.735	3.530	11.840
Andradite, $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ .....	1.895	3.750	12.040

A good example of how X-ray methods may come to the aid of mineralogical description when ordinary crystallographic methods have failed is given in the case of the new mineral aramayoite,<sup>41</sup>  $\text{Ag}(\text{Sb,Bi})\text{S}_2$ . Distinctly developed crystals are not available and from the cleavages it could only be concluded that the mineral was perhaps tetragonal. Laue photographs, taken by (Miss) K. Yardley<sup>42</sup> through the perfect basal cleavage, showed an absence of symmetry, and spectrometer and powder measurements proved the mineral to be triclinic (pseudo-tetragonal). By these means the dimensions of the unit cell and the crystallographic constants were completely determined.

So many workers are now engaged on X-ray research that it often happens that the same mineral has been examined independently several times. For example, the following determinations of the unit orthorhombic cell of baryte ( $\text{BaSO}_4$ ) show a very satisfactory agreement.

<sup>39</sup> *Centr. Min.*, [A], 1925, 344; 1926, 343.

<sup>40</sup> *Amer. Min.*, 1927, 12, 327.

<sup>41</sup> L. J. Spencer, *Min. Mag.*, 1926, 21, 156; *A.*, 1927, 225.

<sup>42</sup> *Min. Mag.*, 1926, 21, 163; *A.*, 1927, 190.



	a.	b.	c.
S. K. Allison <sup>43</sup> .....	4.449	5.448	7.170 Å.
R. W. James and W. A. Wood <sup>44</sup> .....	8.852	5.430	7.132
L. Pauling and P. H. Emmett <sup>45</sup> .....	8.846	5.430	7.10
R. W. G. Wyckoff and H. E. Merwin <sup>46</sup> .....	8.89	5.45	7.17
F. Rinne, H. Hentschel, and E. Schiebold <sup>47</sup> ...	8.88	5.45	7.15
W. Basche and H. Mark <sup>48</sup> .....	8.85	5.45	7.14

With one exception, all these authors agree in taking a double value for the  $a$ -axis, and the axial ratios  $a : b : c$ , usually accepted as 0.8152 : 1 : 1.3136, become 1.6304 : 1 : 1.3136. This means that the rarer prism  $n(120)$  becomes the unit prism instead of the prism parallel to the perfect cleavage, which by crystallographers is naturally taken as a primitive form. The reason for the marked difference in this case is not clear. In this connexion we are reminded of the well-known similarity between the crystal forms of baryte and sulphates, selenates, chromates, perchlorates, and permanganates with the same type of formula, viz.,  $\text{PbSO}_4$ ,  $\text{BaSeO}_4$ ,  $\text{BaCrO}_4$ ,  $\text{KClO}_4$ ,  $\text{KMnO}_4$ , etc. F. Rinne <sup>49</sup> has referred to these as isotypes of the baryte type, and he points out a remarkable relation between the interfacial angles of the crystals. In baryte the mean of the three angles  $(110) : (110) = 78^\circ 22'$ ,  $(011) : (011) = 74^\circ 34'$ ,  $(102) : (102) = 77^\circ 43'$  is  $76^\circ 53'$ ; and in all the other salts the mean of the corresponding angles is, perhaps by a mere coincidence, also  $76^\circ 53'$ . This angle is near to that ( $77^\circ 19'$ ) of the cubic pentagonal-dodecahedron (540), which in combination with the cube closely resembles the baryte habit. The fact that some of these salts change into a cubic modification at a higher temperature is perhaps related to this approximation to cubic angles. Based on the above similarity, A. E. H. Tutton <sup>50</sup> has calculated from the topic axes the dimensions of the unit cells of various perchlorates.

In contrast with the above example of close agreement obtained independently by X-ray workers in different countries, an example may be quoted of lack of agreement. For the indirect determination of density from the structure of mercury telluride (but whether on artificially prepared HgTe or on the mineral coloradoite

<sup>43</sup> *Amer. J. Sci.*, 1924, [v], **8**, 261; *A.*, 1925, ii, 18.

<sup>44</sup> *Mem. Manchester Phil. Soc.*, 1925, **69**, No. 5; *Proc. Roy. Soc.*, 1925, [A], **109**, 598; *A.*, 1926, 13.

<sup>45</sup> *J. Amer. Chem. Soc.*, 1925, **47**, 1026; *A.*, 1925, ii, 485.

<sup>46</sup> *Amer. J. Sci.*, 1925, [v], **9**, 286; *Z. Krist.*, 1925, **61**, 452; *A.*, 1925, ii, 485.

<sup>47</sup> *Z. Krist.*, 1925, **61**, 164.

<sup>48</sup> *Ibid.*, 1926, **64**, 1.

<sup>49</sup> *Centr. Min.*, 1924, 161.

<sup>50</sup> *Proc. Roy. Soc.*, 1926, [A], **111**, 462; *A.*, 1926, 888.

is not in all cases quite clear) the following values have been obtained :

	<i>d.</i>
W. Hartwig <sup>51</sup> .....	8.025
W. F. de Jong <sup>52</sup> .....	8.20
W. Zachariasen <sup>53</sup> .....	8.42

### *Microscopic Examination of Opaque Minerals.*

The examination under the microscope of polished sections of ore-minerals by reflected light, following the methods of metallography, has been much developed during recent years. This subject, or rather method of investigation, has been called "mineralography" or "mineragraphy" in America and "chalcography" (Chalkographie) <sup>54</sup> in Germany. Text-books have been written by J. Murdoch (New York, 1916), W. M. Davy and C. M. Farnham (New York, 1920), H. Schneiderhöhn (Berlin, 1922), and R. W. van der Veen (The Hague, 1925), and a useful outline with detailed bibliography has been given by J. Orceel.<sup>55</sup> Various chemical reagents are applied to the polished surfaces for the purpose of distinguishing one mineral from another. More recently, the method has been extended by the use of polarised light, it being possible to distinguish between isotropic and anisotropic crystals and to determine the directions of the principal axes of refringence and of absorption. The method has been extensively applied in America and Germany to the study of ores and ore-deposits. In addition to identifying the various minerals present in the ore, much can be learnt from their mutual relations and order of deposition.

Various obscure and doubtful metallic minerals examined by this method have been proved to be really mixtures, and the complex chemical formulæ that have been applied to them are thus readily explained. The formula of bornite has been usually given as  $\text{Cu}_3\text{FeS}_3$ ; but the mineral is frequently intergrown with chalcopyrite, chalcosine, etc., and even well-developed crystals often contain a nucleus of chalcopyrite. Recent analyses made on material proved microscopically to be homogeneous have given the formula  $\text{Cu}_5\text{FeS}_4$ .<sup>56</sup> In argentiferous galena it has been shown

<sup>51</sup> *Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1926, 79; *A.*, 1926, 664.

<sup>52</sup> *Z. Krist.*, 1926, 63, 466; *A.*, 1926, 996.

<sup>53</sup> *Norsk Geol. Tidsskrift*, 1926, 8, 302; also *Z. physikal. Chem.*, 1926, 124, 277; *A.*, 1927, 96, where the value 8.123 is given.

<sup>54</sup> The term chalcography has been in use in English since at least the year 1661 for the art of engraving on copper.

<sup>55</sup> *Bull. Soc. franç. Min.*, 1926, 48 (for 1925), 272—361; *Rev. Mét.*, 1926, 23, 537, 618.

<sup>56</sup> J. Orceel, *Bull. Soc. franç. Min.*, 1926, 48 (for 1925), 340.

that the silver is present as specks of tetrahedrite or argentite, or sometimes, in richer samples, as veinlets of ruby-silver. The examination of polished sections of the selenium ores from the Harz Mountains has led to the identification of umangite ( $\text{Cu}_3\text{Se}_2$ ) in addition to the selenium minerals previously known from this locality. In polarised light the umangite shows a strong pleochroism, from cherry-red to grey.<sup>57</sup> The complex intergrowths of arsenides and sulpharsenides of cobalt, nickel, and iron occurring at Cobalt in Ontario have also been studied by this method.<sup>58</sup>

The two modifications of silver sulphide, the cubic argentite and the orthorhombic acanthite, were found by H. Schneiderhöhn<sup>59</sup> in 1922 to be optically anisotropic and both presumably orthorhombic. Crystals of argentite show a complex lamellar structure and are evidently paramorphs after the high-temperature cubic modification, as is the case with leucite. The inversion temperature for silver sulphide is  $180^\circ$ . Similarly, cuprous sulphide is dimorphous as represented by orthorhombic crystals of the mineral chalcosine and by artificially prepared cubic crystals, the latter being stable above  $91^\circ$ . In the copper ores of Tsumeb in South-West Africa, Schneiderhöhn found in 1920 that the chalcosine is of two kinds: (1) a more abundant form with a granular structure and presumably of secondary formation; (2) one showing a complex lamellar structure with an octahedral arrangement, very similar to the structure shown by meteoric irons. The latter he concluded was the primary ore which had crystallised as the cubic modification at a temperature above  $91^\circ$ , and which on cooling passed over into the orthorhombic modification. The presence of "lamellar argentite" or of "lamellar chalcosine" fixes two points ( $180^\circ$  and  $91^\circ$ ) on the "geological thermometer" in any discussion on the origin of ore-deposits. These conclusions, arrived at by the metallographic method, on the dimorphous relations of the silver and cuprous sulphides, have since been amply confirmed by the X-ray method when the materials were examined at different temperatures.<sup>60</sup>

### *Forms of Calcium Carbonate.*

While "conchite" and "ktypeite" are evidently compact forms of aragonite, the artificially prepared vaterite is doubtless distinct from both calcite and aragonite, and it appears to be identical with the  $\mu\text{-CaCO}_3$  of Johnston, Merwin, and Williamson (*Ann. Report*,

<sup>57</sup> G. Frebold, *Centr. Min.*, [A], 1927, 16, 196; J. Olsacher, *ibid.*, p. 170.

<sup>58</sup> E. Thomson, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 54.

<sup>59</sup> *Amer. Min.*, 1927, 12, 210.

<sup>60</sup> F. Rinne, *Z. Krist.*, 1924, 60, 299; L. S. Ramadell, *Amer. Min.*, 1925, 10, 281; R. C. Emmons, C. H. Stockwell, and R. H. B. Jones, *ibid.*, 1926, 11, 326; T. Barth, *Centr. Min.*, [A], 1926, 284.

1917, **14**, 241). More recently, Gibson, Wyckoff, and Merwin<sup>61</sup> find by the X-ray powder method that the spherulitic material, to which the name "vaterite" has been applied, includes two forms: "vaterite A" prepared by the method of Johnston, Merwin, and Williamson is spherulitic calcite; whilst "vaterite B" (i.e., the true vaterite), obtained from colloidal calcium carbonate at 5° in the presence of an excess of potassium carbonate, is  $\mu$ -CaCO<sub>3</sub>. The latter was obtained by Johnston, Merwin, and Williamson as hexagonal plates. F. Heide<sup>62</sup> finds that the gelatinous precipitate given by solutions of *N*/2-potassium carbonate and 2*N*-calcium chloride at 5° changes after 1½—2 hours to minute (3—10  $\mu$ ) radially-fibrous spherulites of vaterite. Heated at 100° in water, this is transformed into calcite, but the dry material is stable up to 430—440°. X-Ray powder photographs show a structure different from that of both calcite and aragonite. The hexagonal cell of vaterite has dimensions  $a = 4.120$ ,  $c = 8.556$  Å., and contains two molecules of CaCO<sub>3</sub>; the calculated density is 2.645. After heating at 430—440°, the material shows the lines of calcite in the X-ray photographs.<sup>63</sup>

At higher temperatures the rhombohedral calcite is the only stable modification, but transformation into  $\alpha$ -CaCO<sub>3</sub> at 970° under pressure in an atmosphere of carbon dioxide was recorded by H. E. Boeke in 1912. Such a transition point could, however, not be found by F. H. Smyth and L. H. Adams,<sup>64</sup> and they placed the melting point of calcite at 1339° under 779,000 mm. pressure. This has an important bearing on the question of the occurrence of primary calcite in igneous rocks, the so-called magmatic calcite, about which there has recently been much discussion. Magmatic carbonate rocks ("carbonatites") were described by W. C. Brøgger (1921) from the Fen district in Norway; and E. Schuster (1919) and R. Brauns (1919) have described calcite-pegmatite and calcite-syenite from the Laacher See district in Rheinland. This has been disputed by N. L. Bowen,<sup>65</sup> who considers that such occurrences represent secondary replacement of silicates, particularly feldspars, by calcite. When limestone rocks are invaded by igneous magmas, there appears no reason why calcium carbonate should not be incorporated in the mass and melted. There is, for example, abundant evidence of this in the pegmatite veins and nepheline-

<sup>61</sup> *Amer. J. Sci.*, 1925, [v], **10**, 325; *A.*, 1925, ii, 1183.

<sup>62</sup> *Centr. Min.*, 1924, 641.

<sup>63</sup> F. Heide, *ibid.*, [A], 1925, 198.

<sup>64</sup> *J. Amer. Chem. Soc.*, 1923, **45**, 1167; *A.*, 1923, ii, 490.

<sup>65</sup> *Amer. J. Sci.*, 1924, [v], **8**, 1; *Centr. Min.*, [A], 1926, 241; *Amer. J. Sci.*, 1926, [v], **12**, 499; and replies by R. Brauns, *Centr. Min.*, [A], 1926, 1 and 245.

syenites of Canada. Some authors<sup>66</sup> have further attempted to prove that such calcite shows peculiarities of structure marking its inversion from  $\alpha$ -CaCO<sub>3</sub> as the temperature fell below 970°, this being taken as a point on the "geological thermometer," in the same way that the change from  $\beta$ -quartz to  $\alpha$ -quartz<sup>67</sup> fixes the point 575°. The distinction appears, however, to be based mainly on lamellar twinning and optical anomalies, such as may be produced artificially in calcite by pressure. The name elatolite<sup>68</sup> has been applied to what is believed to have been  $\alpha$ -calcite leached out of tree-like cavities in the nepheline-syenites of the Kola peninsula in Russian Lapland.

The minerals hydroconite, hydrocalcite (trihydrocalcite, pentahydrocalcite), and lublinitite periodically come to be regarded as doubtful minerals, because when re-examined on museum material they are found to be merely calcite. Hydrated calcium carbonate (CaCO<sub>3</sub>·6H<sub>2</sub>O) is stable only below 5°, and in nature it is but rarely observed in the winter as a mould-like efflorescence on limestone and chalk. To preserve such a mineral a refrigerator would be required. In addition to the hexahydrate,<sup>69</sup> crystals of the pentahydrate have also been prepared; whilst a trihydrate, perhaps stable between 17° and 25°, could not be isolated.<sup>70</sup>

#### *Determinative Tables.*

E. S. Fedorov's method of crystallo-chemical analysis (*Ann. Report*, 1923, 20, 289), on which great hopes were laid, has not come into general use. The symbols he uses are not generally intelligible, and the introduction to his volume "Das Krystallreich" is so written that from the volume itself it is not possible to understand his method. A. K. Boldyrev, in a pamphlet published by the Russian Academy of Sciences,<sup>71</sup> explains doubtful passages in this introduction and gives supplementary explanations for the instruction of the reader. Boldyrev<sup>72</sup> has also published

<sup>66</sup> T. L. Walker and A. L. Parsons, *Univ. Toronto Studies, Geol. Ser.*, 1925, No. 20, 14; J. L. Gillson, *Amer. Min.*, 1927, 12, 357.

<sup>67</sup> Unfortunately there is here some confusion in nomenclature:  $\alpha$ -CaCO<sub>3</sub> or  $\alpha$ -calcite is the high-temperature modification, whilst in quartz the high-temperature modification is denoted as  $\beta$ -quartz and the low-temperature modification as  $\alpha$ -quartz.

<sup>68</sup> A. E. Fersman, 1922—3; *Ann. Report*, 1925, 22, 278.

<sup>69</sup> *Ann. Report*, 1923, 20, 277.

<sup>70</sup> J. Hume, *J.*, 1925, 127, 1036; *A.*, 1925, ii, 697; J. Hume and B. Topley, *J.*, 1926, 2932; *A.*, 1927, 12.

<sup>71</sup> "Kommentarien zum Werk von E. S. Fedorow: 'Das Krystallreich'" [*Russian with German résumé*], Leningrad, 1926, 72 pp. [*Min. Mag. (Abstr.)*, 1927, 3, 326].

<sup>72</sup> *Mém. Soc. Russe Min.*, 1924, 53, 251 [*Min. Mag. (Abstr.)*, 1926, 3, 159].

a criticism of the method in which he points out that there is some difficulty in arriving at the correct complex-symbol. He has therefore suggested and worked out in some detail another method of "crystallo-chemical analysis." This method is based on interfacial angles taken in conjunction with other characters. Some 9000 substances have been entered on catalogue cards and sorted according to the angles in each crystal system. The cards give for each substance: (1) a list of the common crystal forms in the order of their importance, cleavage, twinning, etc.; (2) physical and optical data; (3) the important crystal angles. In the optically uniaxial systems the angles given are those to the basal plane, and in the remaining systems the angles to the axial planes (from which the latitude and longitude,  $\rho$  and  $\phi$ , angles of two-circle goniometry can be deduced if wanted). The method is explained in the French résumé, and sample cards are printed in German in the Russian text. The data have been largely compiled from P. Groth's "Chemische Krystallographie." One of the examples given for the orthorhombic system is "orthorhombic tin" ("β-tin"). If the cards had sorted out properly it would have been noticed that this is identical with stannous sulphide.<sup>73</sup>

Determinative tables or keys of various kinds have long been used in mineralogy. They have been based on obvious external characters, such as lustre, colour, and streak, supplemented by hardness, specific gravity, system of crystallisation, optical characters, etc. In one ingenious device a number of perforated sheets each corresponding with a certain character are laid over a sheet on which are printed the names of minerals until at last the name of the mineral wanted appears in the only opening left. Rule-of-thumb methods of this kind only lead to error, and any table or key must be used with a certain amount of understanding and intelligence. The main use of a table is in suggesting what a given mineral may or may not be, and then some special test must be applied. E. S. Larsen's tables of optical data (*Ann. Report*, 1923, 20, 290) are perhaps the most practical and useful that have yet been devised for determinative purposes. A table of specific gravities may also be a useful aid for the identification of minerals. A recent table<sup>74</sup> gives a numerical list of 2277 determined values collected from the literature for the period 1910—1927; and an alphabetical list of mineral names gives the minimum and maximum values recorded for each mineral.

A useful table might be compiled from the data given by the unit-cell dimensions (in Ångström units) of crystals as determined

<sup>73</sup> Compare *Min. Mag.*, 1921, 19, 113.

<sup>74</sup> L. J. Spencer, *Min. Mag.*, 1927, 21, 337.

by X-ray methods. In such a table, with a numerical arrangement, there would be a considerable differentiation of the various kinds of materials. The X-ray patterns given by the powder method of various known minerals have already been used by several workers as standards for comparison for the purpose of identifying the minerals present in intimate mixtures (*Ann. Report*, 1923, **20**, 282). A reference collection of the X-ray powder patterns of chemically analysed samples of minerals has been commenced in the Department of Geology of the University of Wisconsin.<sup>75</sup>

#### *New Minerals.*

A considerable number of "new" minerals have been described more or less completely since the last Report. The following list is limited to those that appear to be distinctive and well established. The ten lists of new mineral names that have been published at the end of each volume of the *Mineralogical Magazine* since 1897 include all names not recorded in Dana's "System of Mineralogy" (6th ed., 1892) and show a total of 1506 names. These are now all collected together in a general index to the set of volumes.<sup>76</sup>

Undoubtedly many more minerals remain to be discovered, although it is of course not to be expected that all known inorganic compounds will be found in the native state. P. N. Chirvinsky,<sup>77</sup> in a note on the prediction of minerals by mineral synthesis, gives a list of 163 chemical elements and compounds that had been prepared artificially before they were known as minerals. He also gives statistical data of the new minerals described during the past 20 years, and finds that silicates and phosphates predominate.

The suggestive work of the late Baron A. de Schulten might be extended in this connexion. He prepared artificially a number of minerals in a crystallised form and determined the crystallographic and physical constants for the pure compounds. He then proceeded to prepare the analogous compounds in the same isomorphous series. For example, having obtained crystals of artificial monetite,  $\text{CaHPO}_4$ , he then prepared the corresponding compounds in which strontium, barium, or lead takes the place of calcium, and arsenic the place of phosphorus. In this series he determined the crystallographic constants and optical data for  $\text{CaHPO}_4$ ,  $\text{SrHPO}_4$ ,  $\text{BaHPO}_4$ ,  $\text{PbHPO}_4$ ,  $\text{SrHAsO}_4$ , and  $\text{PbHAsO}_4$ . Crystals of  $\text{CaHAsO}_4$  were also obtained but they were too small for measurement. Any of these compounds might be expected to occur in nature, but hitherto

<sup>75</sup> A. N. Winchell, "'Finger Prints' of Minerals," *Amer. Min.*, 1927, **12**, 261.

<sup>76</sup> L. J. Spencer, *Min. Mag.*, 1926, General Index to vols. 11—20 (1895—1925).

<sup>77</sup> P. Tschirwinsky, *Z. Krist.*, 1926, **64**, 544.

only monetite has been known. Recently his "arsenical lead monetite" has been found as a mineral and named schultenite (p. 313 below).

Two recently found minerals, not yet completely described, appear to represent new compounds of palladium. One of them, of sparing occurrence in the diamond washings of British Guiana, was determined by the late Sir John Harrison<sup>78</sup> to be a palladium mercuride with the probable formula  $\text{PdHg}$ . The small silver-white nuggets and grains have a density up to 15.82, i.e., considerably higher than that of either palladium or mercury. This mineral has since been named potarite, from the Potaro River in British Guiana. A palladium antimonide,<sup>79</sup>  $\text{Pd}_3\text{Sb}$ , has been found, in association with fine large crystals of sperryllite<sup>80</sup> ( $\text{PtAs}_2$ ), in the Potgietersrust platinum fields, Transvaal, where minute silver-white grains were detected in pannings of the platinum ore.

Ammoniojarosite<sup>81</sup> is one of the few minerals containing ammonium and is interesting in illustrating the wide range of isomorphous replacement in the jarosite group.

Jarosite .....	$\text{K}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Natrojarosite .....	$\text{Na}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Plumbojarosite .....	$\text{PbO}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Argentojarosite .....	$\text{Ag}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$
Ammoniojarosite .....	$(\text{NH}_4)_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$

Ammoniojarosite was found as small ochre-yellow nodules with tschermigite (ammonium alum) in lignitic shale; and, like all the other members of the group, it comes from Utah. Still another member of the same group is probably carphosiderite,  $\text{H}_2\text{O}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$ . Replacing ferric oxide by alumina, another section of this isomorphous group is represented by alunite and natroalunite. Further, the sulphate may be partly or wholly replaced by phosphate, giving several sulphato-phosphates (beudantite, svanbergite, etc.) and phosphates (hamlinite, florencite, etc.), all of which are closely related crystallographically to jarosite and alunite.

Aramayoite,<sup>82</sup> sulphantimonite and sulphobismuthite of silver,  $\text{Ag}(\text{Sb}, \text{Bi})\text{S}_2$ , is found in a silver-tin vein in Bolivia as iron-black platy aggregates with brilliant metallic lustre on the perfect basal cleavage. It breaks up into square (or nearly square) plates

<sup>78</sup> J. B. Harrison and C. L. C. Bourne, *Off. Gazette Brit. Guiana*, Feb. 27, 1925, No. 71; *A.*, 1925, ii, 593.

<sup>79</sup> H. R. Adam, *J. Chem. Met. Soc. S. Africa*, 1927, 27, 249; *A.*, 851.

<sup>80</sup> L. J. Spencer, *Min. Mag.*, 1926, 21, 94.

<sup>81</sup> E. V. Shannon, *Amer. Min.*, 1927, 12, 424.

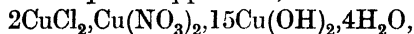
<sup>82</sup> L. J. Spencer, *Min. Mag.*, 1926, 21, 156; *A.*, 1927, 225; E. Kittl, *Revista Minera de Bolivia*, 1927, 2, 53.



bounded at the sides by fibrous pyramidal cleavages. In the absence of definite crystal faces for goniometric measurement, it appeared to be tetragonal, but as determined by X-ray methods<sup>83</sup> it is shown to be triclinic (pseudo-tetragonal), and the crystallographic constants have been completely determined.

*Avogadrite*, potassium fluoborate,  $\text{KBF}_4$ , occurs as minute orthorhombic plates (homœomorphous with baryte,  $\text{BaSO}_4$ ,  $\text{KMnO}_4$ , and  $\text{KClO}_4$ ) in saline sublimations from the floor of the crater of Vesuvius. The detection<sup>84</sup> spectroscopically of notable amounts of cæsium together with potassium in the aqueous extract of these sublimations led to the discovery of the new mineral, and its characters were more completely determined on material recrystallised from this solution.<sup>85</sup> A comparison of the data so obtained with the physical constants of pure potassium fluoborate and of pure cæsium fluoborate suggested that the crystals of avogadrite contained  $\text{KBF}_4$ , 90.5%, and  $\text{CsBF}_4$ , 9.5%. A later crop of recrystallised material gave data ( $d$  2.498,  $n_{\text{Na}}$  1.325) agreeing more closely with those for pure potassium fluoborate.<sup>86</sup> The refractive index is less than that of water.

*Buttgenbachite*,<sup>87</sup> a complex copper salt,



differs from connellite [ $2\text{CuCl}_2, \text{CuSO}_4, 15\text{Cu}(\text{OH})_2, 4\text{H}_2\text{O}$ ] in containing nitrate in place of sulphate. It is found as a fine felt of sky-blue needles with native silver in cavities in cuprite at Likasi, Belgian Congo. The crystals are hexagonal, and buttgenbachite is optically negative, whilst connellite is positive. The two minerals are the end members of an isomorphous series in which mixed crystals occur; previously, W. E. Ford and W. M. Bradley, in 1915, had found 0.72% of  $\text{N}_2\text{O}_5$  in connellite from Arizona.

*Fluoborite*,<sup>88</sup> a fluoborate of magnesium,  $3\text{MgO}, \text{B}_2\text{O}_3 + 3\text{Mg}(\text{F}, \text{OH})_2$ , has been found as colourless hexagonal prisms in an iron mine at Norberg, Sweden.

*Ianthinite*,<sup>89</sup> hydrated uranous oxide,  $2\text{UO}_2, 7\text{H}_2\text{O}$  (?), representing an intermediate alteration product of pitchblende at the Kasolo

<sup>83</sup> (Miss) K. Yardley, *Min. Mag.*, 1926, 21, 163; *A.*, 1927, 190.

<sup>84</sup> F. Zambonini and L. Coniglio, *Atti (Rend.) R. Accad. Lincei*, 1926, [vi], 3, 521; *A.*, 1926, 816. <sup>85</sup> F. Zambonini, *ibid.*, p. 644; *A.*, 1926, 934.

<sup>86</sup> G. Carobbi, *ibid.*, 4, 382; *A.*, 1927, 129.

<sup>87</sup> A. Schoep, *Compt. rend.*, 1925, 181, 421; *Bull. Soc. chim. Belg.*, 1925, 34, 313; *A.*, 1925, ii, 1196; H. Buttgenbach, *Ann. Soc. géol. Belg.*, 1926, 50, Bull. 35; A. Schoep, *ibid.*, 1927, 49 (for 1926), Bull. 308; 1927, 50 (for 1926—7), Bull. 215.

<sup>88</sup> P. Geijer, *Geol. För. Förh.*, 1926, 48, 84; *Årsbok Sveriges Geol. Unders.*, 1927, 20 (for 1926), No. 4.

<sup>89</sup> A. Schoep, *Natuurwetensch. Tijds.*, 1926, 7 (for 1925), 97; *ibid.*, 1927, 9, 1; *Ann. Soc. géol. Belg.*, 1927, 49 (for 1926), Bull. 188, 310.

mine, Katanga, Belgian Congo, forms minute orthorhombic crystals with a micaceous cleavage in one direction. The crystals are black with a violet tinge and semi-metallic lustre; the pleochroism is intense—dark violet to colourless. Some of the crystals are bordered by a yellow zone and others are completely changed to a yellow material. A crystal of ianthinite heated at  $50^{\circ}$  in a drop of water changes from violet to brown and finally to yellow. These yellow alteration products are perhaps becquerelite and schoepite ( $\text{UO}_3 \cdot 2\text{H}_2\text{O}$ ), although they differ from these in their optical characters. The refractive indices<sup>90</sup> of ianthinite are  $n_{\alpha} = 1.674$ ,  $n_{\beta} = 1.90$ ,  $n_{\gamma} = 1.92$ . A specimen acquired in 1922 for the mineral collection of the British Museum has since been identified as ianthinite. It shows a velvet-like pile of minute needles on pitchblende. When acquired, the colour was purple, but now (1927) it is greenish-yellow; crystals that had been mounted in Canada balsam still retain their original colour and intense pleochroism. The change is evidently due to oxidation in the air of a hydrated uranous oxide to a hydrated uranic oxide.

*Kernite*<sup>91</sup> is hydrated sodium borate,  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$ , containing less water of crystallisation than borax. As large orthorhombic crystals and as clear cleavage masses, it has been found in some quantity in bore-holes in Kern Co., California.

*Malladrite*,<sup>92</sup> sodium fluosilicate,  $\text{Na}_2\text{SiF}_6$ , occurs as minute hexagonal prisms, together with hieratite ( $\text{K}_2\text{SiF}_6$ ) in material collected from fumaroles on Vesuvius. The recrystallised material shows regular growths of the cubic potassium salt on the hexagonal sodium salt. Another fluosilicate, cryptohalite  $[(\text{NH}_4)_2\text{SiF}_6]$ , had been previously observed on Vesuvius.

*Schultenite*,<sup>93</sup> lead hydrogen arsenate,  $\text{PbHAsO}_4$ , colourless monoclinic crystals of platy habit, is found on pseudomorphous crusts after mimetite and anglesite at Tsumeb, South-West Africa. The table of angles for the several crystal forms is set out to give the angle from each face to the three axial planes, this method combining the advantages of both the arrangement of interfacial angles in zones and the latitude and longitude angles of two-circle goniometry.<sup>94</sup>

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<sup>90</sup> V. Billiet, *Natuurwetensch. Tijds.*, 1926, 7 (for 1925), 112; *Bull. Soc. franç. Min.*, 1926, 49, 136.

<sup>91</sup> W. T. Schaller, *Amer. Min.*, 1927, 12, 24; H. S. Gale, *Engin. Mining J.*, 1927, 123, 10.

<sup>92</sup> F. Zambonini and G. Carobbi, *Atti (Rend.) R. Accad. Lincei*, 1926, [vi], 4, 171; *A.*, 1926, 1119.

<sup>93</sup> L. J. Spencer, *Nature*, 1926, 118, 411; *A.*, 1926, 1022; *Min. Mag.*, 1926, 21, 149; *A.*, 1927, 225.

<sup>94</sup> Compare A. K. Boldyrev, p. 309 above.

## CHEMICAL KINETICS.

ALTHOUGH in extent the subject of chemical kinetics is expanding almost to constitute a separate and specialised branch of science, its general interest, so far from contracting in proportion, is widening. Indeed, its central problem, the interpretation in physically intelligible terms of the inner mechanism of chemical reaction, is perhaps that which presents the greatest common measure of interest to physicists and to chemists. Since the early days, when the mystery of slow chemical changes first began to attract attention, many lines of advance have been opened, and it is rather striking to observe how practically all of these are still being actively followed. First, there was the quantitative expression of reaction velocities in terms of the law of mass action, and the analysis of stoicheiometric equations into their component parts; the correct representation of reaction velocities in solutions where concentrations and "activities" differ is the modern development of the formal side of this, and the discussions which still continue about the equations expressing the velocity of such common reactions as the union of hydrogen and chlorine show how far the work of van 't Hoff is from completion. Then came the explanation of the remarkable effect of temperature on chemical reaction velocity, the introduction of the idea that only molecules with a certain critical energy can react, and the application of the kinetic theory; all this started with Arrhenius many years ago, and is only now reaching its full development. The drawing of a clear distinction between homogeneous and heterogeneous reactions was an essential step forward. It was followed by the recognition of the fact that the law of mass action has to be applied in a quite different way to heterogeneous reactions; the development of the adsorption theory and its application to the kinetics of surface reactions still proceed rapidly, and attention has lately been directed to the finer points about such reactions, *e.g.*, their relation to the corresponding homogeneous reactions, and the nature of catalytic surfaces. Van 't Hoff found long ago that many gas reactions take place only in contact with the walls of the containing vessel. This led to the belief that no homogeneous gas reactions exist. It is now recognised that they exist, but are comparatively rare. The discovery of new examples continues to be the object of many researches. Thus there is a remarkable historical continuity about most of the aspects of the subject.

The phenomena of chemical change are extraordinarily diverse; and the last few years have seen many theories, perfectly valid for one set of facts, mistakenly applied beyond their proper scope. Their failure when thus misapplied has not infrequently led to an unduly agnostic attitude towards all attempts at theoretical explanation. Three theories, for example, have been proposed about the mechanism of unimolecular reactions, and the suggestion and discussion of each was a definite advance. Two of them appear not to be applicable, and this has caused them to be regarded, in some quarters, as valueless. This judgment, however, is mistaken in its turn, since the ideas contained in each have provided the explanation of quite different classes of reaction.

The phenomena of chemical change are not only diverse but also complex. A result of this is that some of the most important laws are to be distinguished, through a mass of minor complications, as tendencies only. They are not the less important for lack of quantitative exactness; but they can only be recognised by a clear-sighted consideration of the facts as a whole, and recognition is not always immediate. A most striking example of this is to be found in the history of Einstein's law.

The special sections of this Report deal as far as possible with subjects in which definitely clearer views have emerged from the work and discussions of the last year or two. Thus only related groups of investigations have been dealt with. This explains the omission of references to papers which, however important in themselves, are of more specialised interest.

#### *Ionisation and Chemical Action.*

Since the nature of chemical combination is electrical, it is legitimate to inquire whether there is any general and fundamental connexion between chemical reactions and ionisation processes. Ever since the early days of the electron theory experiments to test this have been made from time to time and there is now an accumulation of evidence that any ionisation accompanying ordinary chemical reactions is of a secondary nature.

J. J. Thomson originally suggested that flames were propagated by the emission of electrons from the parts already burning, but extremely few or no ions could be detected in the combination of hydrogen and chlorine (Thomson), the decomposition of ammonia (Kirkby and Marsh), the combination of carbon monoxide and oxygen (de Muijnck), or the combination of hydrogen and oxygen (Haselfoot and Kirkby). Attempts have been made to stop or slow down the propagation of explosions by removing electrons with an electric field (Lind) or with a magnetic field (Dixon, Camp-

bell, and Slater), but with negative results. Malinowski, however, working with feebly explosive mixtures of certain hydrocarbons and air, thought he could suppress the explosion in this way.

A. K. Brewer,<sup>1</sup> using a much more delicate experimental technique, succeeded in measuring the ionisation accompanying a number of reactions, the interaction of nitric oxide and oxygen and of nitric oxide and ozone, and the decomposition of ozone, nitrogen peroxide, and nitrogen pentoxide. One pair of ions was always formed for the reaction of about  $10^{13}$  molecules. Although the ionic current was always proportional to the applied voltage, showing that a good deal of recombination occurred, this proportion is so small as to leave little doubt that the ionisation is of a secondary character. W. E. Garner and S. W. Saunders<sup>2</sup> found that the small ionisation produced in the explosion of hydrogen and oxygen was more or less what might be expected for the purely thermal ionisation at the maximum temperature of the explosion as calculated from Saha's equation. S. W. Saunders and K. Sato<sup>3</sup> measured the conductivity of exploding mixtures of carbon monoxide and oxygen, and Saunders<sup>4</sup> of mixtures of acetylene and oxygen, and of methane and oxygen; the results all indicate that the ionisation is mainly thermal.

The ionisation produced by burning bodies and by the escape of gases from liquids has long been recognised as thermal or mechanical in origin. (The accepted explanation of the ionisation accompanying the oxidation of phosphorus as due to an indirect photoelectric effect has, however, recently been questioned by W. Busse.<sup>5</sup>) The only established example where there is any copious ionisation accompanying a chemical change is the curious reaction between the liquid alloy of sodium and potassium and gases such as carbonyl chloride. Recent experiments of O. W. Richardson and M. Brotherton<sup>6</sup> confirm the view that we have here a unique case of direct chemical ionisation.

There is nothing very puzzling about all these results if we reflect that in chemical reactions between substances not already ionised there is a re-arrangement of the electronic orbits constituting some of the non-polar links in the molecules. While there is no necessity for any electrons to be detached in this process, a few may, in exceptional circumstances, escape, giving rise to the minute ionis-

<sup>1</sup> *J. Amer. Chem. Soc.*, 1924, **46**, 1403; *A.*, 1924, ii, 745.

<sup>2</sup> *Trans. Faraday Soc.*, 1926, **22**, 342; *A.*, 1926, 654, 1205. References to early work are to be found here.

<sup>3</sup> *Ibid.*, 1927, **23**, 248; *A.*, 605.

<sup>4</sup> *Ibid.*, p. 256; *A.*, 605.

<sup>5</sup> *Ann. Physik*, 1927, [iv], **82**, 873; *A.*, 633.

<sup>6</sup> *Proc. Roy. Soc.*, 1927, [A], **115**, 20; *A.*, 713.

ation observed in experiments such as those of Brewer. In Richardson's experiments, it is presumably the free electrons of the metal which escape.

We conclude, then, that, in general, chemical change is in no way dependent upon, or necessarily accompanied by anything more than a small ionisation of a secondary or accidental character.\*

On the other hand, if fast-moving ions or electrons are introduced into or produced in a gas, marked chemical effects may be brought about by their collision with other molecules. A good deal of work has lately been done on this subject.

S. S. Joshi <sup>7</sup> has investigated the decomposition of nitrous oxide in the silent electric discharge (6000—12,500 volts; 150 cycles per second) in respect of the influence of gas pressure and current; E. Warburg and W. Rump <sup>8</sup> have studied the formation of ammonia from its elements in a Siemens tube—though this appears to be largely a catalytic reaction. G. A. Elliott, S. S. Joshi, and R. W. Lunt <sup>9</sup> have worked out expressions for the velocity of a reaction in the silent discharge, assuming that transformation takes place when a gas molecule collides with an ion the kinetic energy of which exceeds a certain critical value. W. K. Hutchison and C. N. Hinshelwood <sup>10</sup> find that ammonia is 5 to 7 times as stable in an electric discharge as nitrous oxide, a fact which is parallel with the greater stability of ammonia to the ordinary molecular impacts which cause the thermal decomposition. G. I. Finch and L. G. Cowen <sup>11</sup> find that for electrolytic gas up to a pressure of 180 mm. there is an inverse proportionality between the pressure and the minimum direct current required to ignite the mixture in a discharge tube. From this they conclude that ignition is determined by the attainment in some portion of the gas of a definite

\* This is a convenient place for an historical observation. In a well-known experiment of H. B. Baker's, a silver wire is heated to its melting point in an initially dry mixture of hydrogen and oxygen. Rapid combination takes place at the surface of the wire but visible drops of water are formed without any explosion in the bulk of the gas. For many years a complete misinterpretation of this experiment has been current in certain text-books, which state that no explosion occurs because the water formed in the experiment is pure and non-conducting. The experiment is supposed to prove some kind of pseudo-electrolytic or "three-body" theory of chemical combination. As we are dealing with ionisation and chemical change, attention may be called to the fact that H. B. Dixon in his Presidential Address to the Chemical Society in 1910 (J., 97, 661) gave the real explanation, which is merely that, by the time drops of water are formed, the wire is surrounded by steam, and there is hardly any hydrogen and oxygen left to explode.

<sup>7</sup> *Trans. Faraday Soc.*, 1927, 23, 227; A., 635.

<sup>8</sup> *Z. Physik*, 1926, 40, 557; A., 1927, 215.

<sup>9</sup> *Trans. Faraday Soc.*, 1927, 23, 57; A., 212.

<sup>10</sup> *Proc. Roy. Soc.*, 1927, [A], 117, 131.

<sup>11</sup> *Ibid.*, 116, 529; A., 1146.

concentration of ions, and make the generalisation, which scarcely seems justified, that flame propagation is essentially an electrical phenomenon. H. F. Coward and E. G. Meiter,<sup>12</sup> studying the ignition of methane by spark discharges, conclude that the spark acts simply as a source of thermal energy.

A. L. Hughes and A. M. Skellett<sup>13</sup> have studied the rate of production of atomic hydrogen by electrons of energy considerably greater than the critical dissociation value. The rate is directly proportional to the pressure, whence they conclude that dissociation depends upon a simple collision between an electron and a molecule. The combination of nitrogen and hydrogen under the influence of thermions has been measured by A. Caress and E. K. Rideal,<sup>14</sup> who suggest that reaction may occur in several different ways, catalytically, and through the agency of hydrogen ions, ionised nitrogen molecules, and atoms, produced respectively at successively increased voltages.

Experiments of a rather different kind have been made by E. Rabinowitsch<sup>15</sup> who attempted to decompose solid metallic oxides by the impact of electrons. He finds that electrons with 1000 times the velocity corresponding to the heat of formation of the oxides have an efficiency of the order of only one in 400 in decomposing the oxides.

Having considered reactions in the gaseous and solid states, we come to catalytic surface reactions. N. R. Dhar, in a theoretical paper,<sup>16</sup> revives the idea that in the adsorption of gases by solid catalysts, ions and electrons are produced and are the active chemical agents. G. I. Finch and J. C. Stimson,<sup>17</sup> following up some earlier work of H. Hartley,<sup>18</sup> have examined the electric charge imparted to metal surfaces by gases. They measured the time-charge and temperature-charge curves for  $H_2$ ,  $O_2$ ,  $CO$ ,  $CO_2$ ,  $H_2O$ , and for the mixtures  $2H_2 + O_2$  and  $2CO + O_2$  in contact with silver and gold up to  $850^\circ$ . One of the most interesting results is that at higher temperatures the curves for steam and for carbon dioxide are the same as those for  $2H_2 + O_2$  and for  $2CO + O_2$ , respectively, indicating that there is dissociation of water and of carbon dioxide on the surface. The charged molecules on the surface are referred to as "active" molecules, but it is very much to be doubted whether they have any connexion with chemically active molecules. The

<sup>12</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 396; *A.*, 318.

<sup>13</sup> *Physical Rev.*, 1927, [ii], **30**, 11; *A.*, 811.

<sup>14</sup> *Proc. Roy. Soc.*, 1927, [A], **115**, 684; *A.*, 943.

<sup>15</sup> *Z. Elektrochem.*, 1927, **33**, 185; *A.*, 708.

<sup>16</sup> *Z. anorg. Chem.*, 1926, **159**, 103; *A.*, 1927, 216.

<sup>17</sup> *Proc. Roy. Soc.*, 1927, [A], **116**, 379; *A.*, 1135.

<sup>18</sup> *Ibid.*, 1914, [A], **90**, 61; *A.*, 1914, ii, 330.

magnitude of the charge is independent of the gas pressure for all the gases; this is very different from the reaction-velocity relationships. The results are interesting but it is probable that their relation to catalytic phenomena will be found to be a very complex one.

*Reproducibility of Reaction Rates: Influence of Moisture and Other Impurities.*

Examples are known of chemical and physical effects which are only produced in the presence of a trace of "impurity." The glowing of active nitrogen is apparently a phenomenon of this kind.<sup>19</sup> The stability of hydrogen peroxide in aqueous solution is very variable, and F. O. Rice and M. L. Kilpatrick<sup>20</sup> have recently explained this by showing that under ordinary circumstances the rate of decomposition is mainly determined by the catalytic action of dust particles. The rate of corrosion of metals is extremely sensitive to impurities. Facts like these make it legitimate to raise the question whether chemical reaction velocities in general have any absolute significance. Several considerations, however, show that more often than not they have. First, it is quite easy to ascertain whether the reaction velocity in any given example is reproducible or not, and the lack of reproducibility which would indicate dependence on traces of impurity is very far from being the general rule. Secondly, the rates of certain reactions calculated theoretically are not only in too close agreement absolutely with the experimentally observed values, but these values exhibit too coherent a relationship among themselves to leave much probability in the hypothesis of accidental catalysis.

It is really a matter of the greatest ease for an experimenter to decide whether he is dealing with a reaction of the "reproducible" or of the "non-reproducible" class, but perhaps not quite easy to convince those who are not in direct experimental contact with the matter. Fortunately, therefore, one of the most discussed reactions of recent years, the decomposition of nitrogen pentoxide, has been investigated under a great variety of circumstances by investigators in different parts of the world, and it is now possible to compare their results. H. S. Hirst<sup>21</sup> found a velocity coefficient of  $7.11 \times 10^{-3}$  at 35.4, compared with the value  $7.71 \times 10^{-3}$  calculated for this temperature from the data of F. Daniels and

<sup>19</sup> K. F. Bonhoeffer and G. Kaminsky, *Z. physikal. Chem.*, 1927, **127**, 385; A., 801.

<sup>20</sup> *J. Physical Chem.*, 1927, **31**, 1507; A., 1154.

<sup>21</sup> *J.*, 1925, **127**, 657; A., 1925, ii, 554.



E. H. Johnston.<sup>22</sup> The results of E. C. White and R. C. Tolman<sup>23</sup> can be compared with those of Daniels and Johnston over a range of temperatures :

Temp.	20°	25°	35°	40°
$k \times 10^5$ (W. & T.) .....	103	219	837	1480
$k \times 10^5$ (D. & J.) .....	117	203	808	1510

More recently a very complete study of the matter has been made by F. O. Rice and D. M. Getz.<sup>24</sup> At 65°, they find  $k = 0.286$ , compared with the value 0.292 of Daniels and Johnston. In order to test the possibility that the reaction might depend on catalysis by dust, they compared the velocity coefficients for filtered and unfiltered nitrogen pentoxide and for gas which had been passed through an electrical dust precipitator. In some experiments the gas was dried with phosphorus pentoxide, in others not. Since all previous workers had prepared the nitrogen pentoxide by the dehydration of nitric acid with phosphorus pentoxide, and since the gas might therefore always have contained the same impurity in the same amount—although this supposition is unlikely enough—they also used nitrogen pentoxide prepared by the action of chlorine on silver nitrate. Finally they showed that there was no evidence of any catalytic effect of nitric acid on the decomposition. The principal results of these experiments are illustrated by the table given below, all data referring to 65° :

	<i>k</i> .
" Ordinary runs " .....	0.286
Gas filtered through blue asbestos .....	0.284
Gas passed through electrical precipitator .....	0.278
P <sub>2</sub> O <sub>5</sub> in reaction vessel .....	0.278
N <sub>2</sub> O <sub>5</sub> made from AgNO <sub>3</sub> and chlorine .....	0.291

Last year, doubt was cast upon the validity of Bodenstein's classical work on the bimolecular gas reactions involved in the formation and decomposition of hydrogen iodide. B. Lewis and E. K. Rideal<sup>25</sup> stated that when hydrogen iodide decomposed in presence of phosphorus pentoxide, it gave, not the equilibrium mixture, but hydrogen and iodine corresponding to complete decomposition. This was taken to prove that drying inhibited the union of the elements but not the dissociation of the compound. If this were correct, Bodenstein's measurements of the rate of union would lose any absolute significance, and, incidentally, the second law of thermodynamics would be untrue. M. Bodenstein and W. Jost,<sup>26</sup> however, point out that the results are entirely

<sup>22</sup> *J. Amer. Chem. Soc.*, 1921, **43**, 53; *A.*, 1921, ii, 249.

<sup>23</sup> *Ibid.*, 1925, **47**, 1240; *A.*, 1925, ii, 682.

<sup>24</sup> *J. Physical Chem.*, 1927, **31**, 1572.

<sup>25</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 2553; *A.*, 1926, 1111.

<sup>26</sup> *Ibid.*, 1927 **49**, 1416; *A.*, 737.

accounted for by chemical reaction between the phosphorus pentoxide and the heated gases.

The thermal decomposition of ozone is an important reaction about which our knowledge at the moment is not as certain as might be desired, and there is some discrepancy between the results of different observers. The inhibiting effect of oxygen, originally found by Jahn and not found by Chapman and Jones, is now found again by O. R. Wulf and R. C. Tolman,<sup>27</sup> who suggest that the oxygen of Chapman and Jones contained a catalyst which counterbalanced the effect of the oxygen itself. They find a certain variation in the velocity coefficients for different samples of gas, not so great, however, as to prevent them from inferring what is probably the true value from a consideration of all their results. It must not be forgotten that this reaction, although predominantly homogeneous, is on the verge of being heterogeneous; and indeed, with certain kinds of glass the wall-reaction predominates. It is still not quite clear that some of the difficulties do not arise from this cause.

Discussion still continues about the necessity for moisture in chemical change, but there is no longer any general belief in it as a "universal catalyst." The view is spreading that the most common cause of inhibition by drying is the removal of a catalytically active film of moisture from a boundary surface in a reaction between two phases, or from the wall of the containing vessel in gaseous reactions such as the combination of ethylene and bromine.<sup>28</sup> It is probable that the union of ammonia and hydrogen chloride is a surface reaction, catalysed by glass covered with a layer of adsorbed water molecules.<sup>29</sup> In these circumstances the influence of the first trace and the ineffectiveness of additional amounts of water are readily understandable. Other polar substances would have almost certainly the same effect as water, the rôle of which is most probably not unique. Nearly all the examples of inhibition by drying, which have been collected during the last few decades, are heterogeneous reactions of one kind or another. The only homogeneous reactions, apart from explosions, which have been stated to be retarded by drying are those between nitric oxide and oxygen and between hydrogen and chlorine. With regard to the first, E. Briner,<sup>30</sup> reviewing all the work that has been done on the

<sup>27</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 1183, 1202; **A.**, 631.

<sup>28</sup> E. J. Bowen, *J.*, 1924, **125**, 1233; *A.*, 1924, ii, 540; R. G. W. Norrish, *Trans. Faraday Soc.*, 1926, **21**, 575; *A.*, 1925, ii, 1080; **A.**, 1926, 584. Compare also O. M. Reiff, *J. Amer. Chem. Soc.*, 1926, **48**, 2893; **A.**, 1927, 57.

<sup>29</sup> Unpublished experiments of R. E. Burk, summarised by C. N. Hinshelwood, "School Science Review," 1927, p. 169.

<sup>30</sup> *J. Chim. physique*, 1926, **23**, 848; **A.**, 1927, 214.

reaction, concludes that, although water can catalyse the reaction, it is not essential to it. The second reaction is a photochemical chain reaction of great complexity, in which it is not certain whether any of the stages are heterogeneous; nor is it certain whether adsorbed water on the walls, or water in the gas phase is the active agent. The results quoted above in connexion with nitrogen pentoxide seem to show that water can play no part in its decomposition. The pentoxide is an "auto-drying" substance, probably more markedly so than phosphorus pentoxide, and any trace of water would probably form nitric acid. If a trace of nitric acid and the still smaller trace of water in equilibrium with it were necessary for reaction, the rate would be proportional to the nitric acid content. Rice and Getz, however, find that nitric acid is not a catalyst for the decomposition. Moreover, the rate of reaction approaches the maximum that can be accounted for on any molecular hypothesis (see next section), so that if the calculated rate had to be cut down some thousands of times to allow for the chance of collision between molecules of pentoxide and molecules of water present in excessively minute concentration, it looks at present as if any idea of interpreting the facts would have to be abandoned.

With regard to gaseous explosions, water vapour has long been known to catalyse the reaction between carbon monoxide and oxygen in the flame or in the explosion wave. Dixon showed that this was due to indirect oxidation by way of the water-gas reaction. F. R. Weston<sup>31</sup> has recently investigated the conditions both of the direct and of the indirect oxidation. He finds from spectroscopic examination of the flames that both reactions are possible, as Dixon supposed. Water, although providing an easier reaction path in this instance, is by no means essential; indeed at higher pressures the direct oxidation tends to predominate.\*

W. E. Garner and C. H. Johnson<sup>32</sup> have examined the infra-red spectra of wet and dry carbon monoxide burning in oxygen. They find that small amounts of water vapour, which increase the rate of reaction, depress the infra-red emission, and suggest that the water increases the rate of reaction by causing more energy to be retained in the system.

### *Unimolecular Gas Reactions.*

There are only three possible reasons why a unimolecular chemical reaction should take place slowly. Either the molecules must be

\* Compare also C. F. R. Harrison and J. P. Baxter, *Phil. Mag.*, 1927, [vii], 3, 31; *A.*, 211.

<sup>31</sup> *Proc. Roy. Soc.*, 1925, [A], 109, 176, 523.

<sup>32</sup> *Phil. Mag.*, 1927, [vii], 3, 97; *A.*, 184.

in a suitable internal phase before they can react, or they must wait their turn to come into contact with a catalyst present in small concentration, or they must be "activated" by the acquisition of energy. Since Arrhenius explained the law of variation of reaction velocity with temperature in terms of "active molecules" it has been recognised that the third condition is the essential one, whether or not the other two come into play as well. The law in question is  $\log k = C - E/RT$ , where  $C$  is a constant, and  $E$  is the "energy of activation," the form of the equation being explained by the fact that, according to the kinetic theory, the fractional number of molecules which possess energy, of any kind, exceeding  $Q$  is  $e^{-Q/RT}$  multiplied by a factor which does not vary very much with temperature.  $Q$  is thus nearly the  $E$  of the Arrhenius equation, there being a correction which is usually not very large. The nature of the energy of activation,\* and the method by which it is communicated to molecules is now the important question. With bimolecular gas reactions it is plausible to assume that the kinetic energy of the impact between the two molecules provides the energy of activation, and on this assumption we find for the number of molecules reacting: (number of collisions)  $\times e^{-E/RT}$ . This equation, in five out of the six known examples, is as nearly true as experiment can decide—within a factor of three or four times.<sup>33</sup> Thus there is no absolute necessity to look any further for the interpretation of bimolecular reactions.

As is well known, unimolecular reactions presented a more difficult problem. J. Perrin's argument<sup>34</sup> that collisions could play no part, and that therefore absorption of radiation must be the cause of reaction, provoked two important suggestions for mechanisms whereby molecules might be activated by collision and yet react according to a unimolecular law. F. A. Lindemann<sup>35</sup> showed that if a molecule received energy by collision but could not decompose until it passed through some suitable internal phase, before which it would most frequently lose its excess energy

\* In view of several statements in the literature of the last year, it is not irrelevant to point out that the energy of activation, or critical energy, is a characteristic of a reaction, not of a substance. There is an energy of activation for the bimolecular homogeneous decomposition of hydrogen iodide, another for its catalytic decomposition in contact with gold, and yet another for the catalytic decomposition by platinum; but to speak of the energy of activation of hydrogen iodide is meaningless.

<sup>33</sup> W. C. McC. Lewis, *J.*, 1918, 113, 471; *A.*, 1918, ii, 263; C. N. Hinshelwood, "Kinetics of Chemical Change in Gaseous Systems," 1926; R. C. Tolman, *J. Amer. Chem. Soc.*, 1925, 47, 1524; *A.*, 1925, ii, 799; J. A. Christiansen, *Proc. Camb. Phil. Soc.*, 1926, 23, 438.

<sup>34</sup> *Ann. Physique*, 1919, [ix], 11, 5; *A.*, 1919, ii, 177.

<sup>35</sup> *Trans. Faraday Soc.*, 1922, 17, 598.

again in a second collision, then the reaction would appear unimolecular over a large range of pressure. At low pressures, however, where the time lag between activation and reaction became commensurate with the average time between collisions, the velocity coefficient would begin to decrease. J. A. Christiansen and H. A. Kramers<sup>36</sup> showed that if "activated" molecules of the products of a reaction could pass on their energy and immediately activate fresh molecules of the reacting substance, thus giving rise to a "reaction chain," then also the reaction will follow the unimolecular law.

The radiation theory will not be discussed here in detail: it fails in two ways—first, because of the inadequacy of the amount of radiation in an isothermal system to provide the energy of activation at the required rate, and secondly, because experiments on the acceleration of reactions by irradiation with the appropriate infra-red radiation lead to negative results. The latest investigation of this kind is that of G. N. Lewis and J. E. Mayer,<sup>37</sup> the reaction studied being the racemisation of pinene in the gaseous state. The pinene was passed at low pressure through a vessel intensely irradiated with infra-red radiation. The result was that none of the racemisation which would have been expected from the theory took place.

Lindemann's mechanism demands that the velocity coefficient shall fall at low pressures, but does not predict at what pressure the effect should begin to be noticeable, since this depends upon a specific factor, namely, the average life of an activated molecule. Two years ago the only unimolecular reaction known was the decomposition of nitrogen pentoxide. H. S. Hirst and E. K. Rideal<sup>38</sup> found that at low pressures the velocity coefficient did not diminish but actually increased. J. H. Hibben,<sup>39</sup> however, now finds that there is no such increase, but that at pressures between 0.2 and 0.002 mm. the velocity coefficient is the same as that found by Daniels and Johnston for normal pressures. The question appears to be open: it must be remarked that the difficulties of avoiding interference by surface reactions at such low pressures must be very great indeed. The discrepancy between the results of Hirst and Rideal and those of Hibben may be due to some such cause.

Several new examples of unimolecular reactions have, however, now been discovered: the decomposition of gaseous acetone<sup>40</sup>

<sup>36</sup> *Z. physikal. Chem.*, 1923, **104**, 451; *A.*, 1924, ii, 28.

<sup>37</sup> *Proc. Nat. Acad. Sci.*, 1927, **13**, 623; *A.*, 948.

<sup>38</sup> *Proc. Roy. Soc.*, 1925, [A], **109**, 526; *A.*, 1926, 32.

<sup>39</sup> *Proc. Nat. Acad. Sci.*, 1927, **13**, 626; *A.*, 948.

<sup>40</sup> C. N. Hinshelwood and W. K. Hutchison, *Proc. Roy. Soc.*, 1926, [A], **111**, 245; *A.*, 1926, 691.

and the racemisation of pinene<sup>41</sup> were the first, and neither of them was investigated with respect to the decrease in the velocity coefficient at low pressures. The decomposition of gaseous propaldehyde<sup>42</sup> then proved to be a homogeneous reaction, following the unimolecular law at higher pressures, but falling off in rate at pressures below about 80 mm. The decompositions of diethyl ether<sup>43</sup> and of dimethyl ether<sup>44</sup> are similar, the rate of reaction being independent of the initial pressure above about 150 mm. for the first, and above about 300 mm. for the second. These reactions thus appear to behave in the manner predicted by Lindemann's theory. A remarkable fact about all three is that in presence of a sufficient concentration of hydrogen the velocity coefficient does not diminish but retains its normal value exactly. This can hardly be attributed to a direct chemical effect of the hydrogen, since it can only keep the coefficient at the normal value and cannot increase it beyond that. In keeping with this, W. F. Busse and F. Daniels<sup>45</sup> find that the nitrogen pentoxide reaction, where the coefficient does not show the diminution, is totally uninfluenced by hydrogen. The hydrogen thus appears to act merely by keeping up the Maxwell distribution of energy among the molecules of the reacting gas, when the supply of active molecules would otherwise begin to fall short of that required to keep the coefficient constant. All this is in complete accordance with the theory; but it is remarkable that the action of hydrogen is so specific, and that helium, nitrogen, and other gases do not have a similar effect. There is, however, great specificity in energy transfers between gas molecules. To quote an example of quite a different kind, the fluorescence of mercury vapour under certain conditions can be reduced to one-half by 0.2 mm. of hydrogen, but only by 30 mm. of nitrogen.<sup>46</sup> Again argon and nitrogen have little effect on the decomposition of ammonia sensitised to the 2537 line by mercury vapour, but small amounts of hydrogen have a large retarding effect.<sup>47</sup> The de-activating action of oxygen in the chlorine-hydrogen combination is another example, since it

<sup>41</sup> D. F. Smith, *J. Amer. Chem. Soc.*, 1927, **49**, 43; **A.**, 212.

<sup>42</sup> C. N. Hinshelwood and H. W. Thompson, *Proc. Roy. Soc.*, 1926, [A], **113**, 221; **A.**, 1927, 26; C. N. Hinshelwood and P. J. Askey, *ibid.*, 1927, [A], **116**, 163; **A.**, 1036.

<sup>43</sup> C. N. Hinshelwood, *ibid.*, 1927, [A], **114**, 84; **A.**, 212.

<sup>44</sup> C. N. Hinshelwood and P. J. Askey, *ibid.*, 1927, [A], **115**, 215; **A.**, 630.

<sup>45</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 1257; **A.**, 635.

<sup>46</sup> H. A. Stuart, *Z. Physik*, 1925, **32**, 262; **A.**, 1925, ii, 629; R. Mannkopff, *ibid.*, 1926, **36**, 315; **A.**, 1926, 557.

<sup>47</sup> A. C. G. Mitchell and R. G. Dickinson, *J. Amer. Chem. Soc.*, 1927, **49**, 1478; **A.**, 739.

is not at all certain that the inhibiting effect is due to removal of atomic hydrogen as Nernst suggested.

Another unimolecular reaction which behaves in accordance with the theory has been discovered by H. C. Ramsperger,<sup>48</sup> in the decomposition of azomethane. The constant does not diminish as soon as in the other examples: at 290°  $k$  at 0.259 mm. has fallen to one-fourth of its value at 707.9 mm., and at 330° over the same pressure range it falls to one-tenth.

There appears thus to be a definite class of reactions to which Lindemann's theory applies; it is significant that all involve molecules of fairly complex structure, for which a time lag between activation and reaction is not improbable *a priori*. Whether the nitrogen pentoxide decomposition belongs to this class is at present an open question, at least as far as the experimental evidence goes.

### *Nature of the Energy of Activation.*

We have already seen that there is general agreement that the rate of nearly all bimolecular gas reactions could be accounted for by assuming that the energy of activation is the translational kinetic energy of a "head-on" collision—whether or not this is the only possible hypothesis. This means, in the language of the kinetic theory, that the total energy of activation is in two degrees of freedom, being made up of the sum of the components of the kinetic energy of each molecule along the line of approach.\* For two degrees of freedom of translational energy, the fractional number of molecules—or pairs of molecules in collision, regarded as one system—which have a total energy greater than  $E$  is exactly given by the factor  $e^{-E/RT}$ , and the maximum possible rate of reaction is  $Z \cdot e^{-E/RT}$ , where  $Z$  is the collision number.

Unimolecular reactions in general proceed at a rate many times greater than this expression requires, *e.g.*,  $10^5$  for the decomposition of acetone,<sup>36, 40</sup> a fact which at first sight seemed very difficult to explain. The difficulty can be surmounted by taking into account all the internal degrees of freedom of the molecule. When this is done, a very much greater possible rate of activation is found.<sup>49</sup> The way this comes about is as follows. When energy

\* The older idea of separate values  $E_1$  and  $E_2$  for each molecule disappears in this way of regarding the matter.

<sup>48</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 912, 1495; **A.**, 425, 737.

<sup>49</sup> G. N. Lewis and D. F. Smith, *ibid.*, 1925, **47**, 1508; **A.**, 1925, ii, 799; C. N. Hinshelwood, *Proc. Roy. Soc.*, 1926, [*A*], **113**, 230; **A.**, 1927, 26; R. H. Fowler and E. K. Rideal, *ibid.*, 1927, [*A*], **113**, 570; **A.**, 114; J. A. Christiansen, see Ref. 33.

in a large number of internal degrees of freedom can count as activation energy, a total  $E$  can be made up in a great many ways owing to the enormous number of possible permutations. Thus the number of molecules with energy greater than  $E$  comes out to  $e^{-E/RT} \cdot (E/RT)^{n-1} / (\frac{1}{2}n - 1)$ , which, for large values of  $n$ , is much greater than the fraction  $e^{-E/RT}$  for two degrees of freedom only;  $n$  is the total number of energy terms. (There are *two* energy terms for each vibrational degree of freedom, since, as Fowler points out, there is no reason why potential energy should not count.) The important thing about this expression is that although it may be much greater than the simple exponential factor, the temperature coefficient is about the same. Thus the calculation of  $E$  from the Arrhenius equation is not much altered, there being a correction of  $(\frac{1}{2}n - 1)RT$  only. When, therefore, many degrees of freedom participate in the activation process, we can have a much greater maximum rate of reaction for the same experimental value of  $E$ .

For those unimolecular reactions of which  $k$  decreases below a certain pressure, an idea can be obtained of the number of energy terms involved. It may be assumed that, at the point where the diminution starts, the rate of activation is just great enough to keep up the normal rate of reaction. (This is merely an approximation, of course.) In this way it can be found that about 12 energy terms\* are needed to account for the behaviour of propaldehyde, 8 for that of diethyl ether, and 11 for that of dimethyl ether. That is to say, 4 to 6 internal vibrations might be involved, which is a plausible enough result.

Fowler and Rideal calculate that even at the lowest pressures there are enough collisions to account for the rate of reaction, but only if the assumption is made that all the energy of two colliding molecules can flow into one of them. They consider this assumption, though not proven, as not impossible. It would be valid if the effective radius of a molecule for de-activation were very many times greater than for activation, as is easily shown. On the face of it, this condition seems an unlikely one, although to explain the variation with pressure of the polarisation of the resonance radiation of mercury vapour, the effective radius of the mercury atom has to be assumed many times greater than that indicated by the kinetic theory.<sup>50</sup>

The following table shows how the unimolecular reaction mechanism tends to be characteristic of molecules with a more complex structure.

\* In some of the original papers these are inaccurately referred to as degrees of freedom.

<sup>50</sup> V. von Keussler, *Ann. Physik*, 1927, [iv], 82, 793; A., 491.



*Unimolecular* : Decomposition of  $\text{N}_2\text{O}_5$ ,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$ ,  $\text{C}_2\text{H}_5\cdot\text{CHO}$ ,  $\text{C}_2\text{H}_5\cdot\text{O}\cdot\text{C}_2\text{H}_5$ ,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_3$ ,  $\text{CH}_3\cdot\text{N}=\text{N}\cdot\text{CH}_3$ ; racemisation of  $\text{C}_{10}\text{H}_{16}$ .

*Bimolecular* : Decomposition of  $2\text{HI}$ ,  $\text{Cl}_2\text{O}$ ,  $\text{N}_2\text{O}$ ,  $\text{O}_3$ ,  $\text{CH}_3\cdot\text{CHO}$ .

Finally, it should be mentioned that Sir J. J. Thomson<sup>51</sup> has put forward a theory of unimolecular reactions based upon the idea that the internal energy of a molecule may fluctuate even in the absence of collisions or of absorption or emission of radiation. The principle of the conservation of energy is abandoned except as a statistical result. Whilst the development of this idea will be watched with great interest by chemists, they will perhaps hardly venture to apply it yet, while there is a chance that their problems may be solved without the introduction of new physical principles.

### *Bimolecular Gas Reactions.*

If the theories outlined in the last two sections about the activation of molecules prove to be generally applicable, the distinction between unimolecular and bimolecular gas reactions will become one of degree only.\* Molecules of simple structure, with a small enough time-lag between activation and transformation, will react at once at a rate proportional to the collision number and thus give second-order reactions; more complex ones suffer many de-activations and thus give first-order reactions. It has been pointed out<sup>42</sup> that two independent facts indicate the soundness of this way of regarding the matter. First, the approximate correctness of the calculation of bimolecular reaction rates from the simple exponential formula for activation in only two energy terms indicates that the activation process is one free from complication, and therefore unlikely *a priori* to be attended with a time-lag. Secondly, the bimolecular nature of the reaction shows *a posteriori* that there is no such time-lag.

The decomposition of ozone appears to be a bimolecular process in which rather more energy terms are involved than two of translational energy.<sup>52</sup> The heat of activation is, according to recent determinations, rather greater than could be supplied by simple impact. This reaction would appear therefore to be of a transitional character, and it is perhaps not without significance that it shows retardation by oxygen, and acceleration by hydrogen, and to a smaller extent by helium and argon.<sup>52</sup> It is also stated that chlorine

\* This does not apply of course to bimolecular reactions where two molecules are necessary for the reaction to be *chemically* possible.

<sup>51</sup> *Phil. Mag.*, 1927, [vii], 3, 241; *A.*, 212.

<sup>52</sup> J. W. Belton, R. O. Griffith, and A. McKeown, *J.*, 1926, 3153; *A.*, 1927, 114; O. R. Wulf and R. C. Tolman, *J. Amer. Chem. Soc.*, 1927, 49, 1650; *A.*, 834.

retards the reaction at lower temperatures and accelerates it at higher temperatures.<sup>53</sup>

### *Chain Reactions.*

The idea of chain reactions originated in two ways. In one form it was introduced to explain the enormous deviation of the hydrogen-chlorine combination from Einstein's law; and chain reactions are now generally supposed to occur wherever many molecules are transformed per quantum absorbed in a photochemical reaction. Weigert and Kellermann obtained direct evidence of the propagation of these chains, and more recently F. Porter, D. C. Bardwell, and S. C. Lind<sup>54</sup> have found striking confirmatory evidence. Over a wide range of conditions they have shown that the relative amounts of combination of hydrogen and chlorine, provoked by light and by  $\alpha$ -particles, are the same. This is strong evidence for the propagation of a definite thermal chain, for, as they say, we have "two entirely distinct physical agents, light and  $\alpha$ -particles, acting through different primary steps, excitation and ionisation, producing total reaction greatly in excess of the unit quantities involved in the primary steps, and yet the total quantities of action referred back to the unit in each case are equal to each other."

In a different connexion the chain mechanism was introduced by Christiansen and Kramers<sup>55</sup> to account for a kinetically unimolecular reaction with activation by collision, and to overcome the difficulty then felt about accounting for the rate of activation. Although the theory has not on the whole found favour in this particular application—it is, however, by no means disproved—Christiansen<sup>55</sup> has applied it further in developing a theory of negative catalysis. A reaction chain is set up by the handing on of energy from "hot" molecules of reaction product to molecules of the reacting substance which thereby become activated and react in their turn. According to the theory, if a substance is capable of breaking such a chain by taking away the energy from one of the "hot" molecules, then it can act as a negative catalyst. Although all examples of negative catalysis are certainly not of this kind, H. L. J. Bäckström<sup>56</sup> has recently found interesting evidence that such processes do occur. In the photochemical oxidation of benzaldehyde, heptaldehyde, and of solutions of

<sup>53</sup> A. Pinkus and A. Radbill, *Bull. Soc. chim. Belg.*, 1926, **35**, 451; *A.*, 1927, 320.

<sup>54</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 2603; *A.*, 1926, 1111.

<sup>55</sup> *J. Physical Chem.*, 1924, **28**, 145; *A.*, 1924, ii, 242.

<sup>56</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 1460; *A.*, 737. Also *Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927, **6**, Numbers 15 and 16; *A.*, 1151.

sodium sulphite, there are very high quantum yields, amounting respectively to 10,000, 15,000, and 50,000 molecules per quantum. This shows that the light probably sets up chain reactions, and the question arises whether chains are set up in the dark reactions also. The photochemical reactions are markedly subject to the action of inhibitors, which presumably cut short the chains, and the important point is that the dark reactions are subject to the influence of the same inhibitors in an almost exactly parallel way. It looks, therefore, as though we have here an example of chain mechanisms in ordinary thermal reactions.

In connexion with the question as to whether chains occur in the decomposition of nitrogen pentoxide, it should be mentioned that no inhibitors are known for its decomposition. Busse and Daniels<sup>45</sup> find that not only hydrogen, but also carbon monoxide, bromine, and chlorine are without influence on the reaction, whilst certain organic vapours promote rapid decomposition and are themselves attacked.

#### *Reactions in Solution.*

There are several striking facts of a general character about reactions in solution. First, as Menshutkin showed long ago, the velocity of a reaction may vary several hundredfold with change of solvent. No general explanation of this has been found, and it must be concluded that reaction rates are subject to highly specific influences of solvent molecules.\*

Secondly, if we assume that the frequency of collision between molecules A and B is of the same order of magnitude in solution as at corresponding concentrations in the gaseous state, and further that the heat of activation is a simple quantity determinable directly from the temperature coefficient, then, as Christiansen has pointed out,<sup>57</sup> the effectiveness of collisions in bimolecular reactions is several powers of ten smaller in solution than in gases. The assumptions, especially the second, are, of course, not free from uncertainty as regards any single example, but from the fact that the result is a general one we must conclude that a large proportion of de-activations occur in solution. In this connexion it is perhaps significant that in several unimolecular reactions, where the rate of activation and de-activation does not come into the expression for the rate of reaction as long as it is large enough, the velocity

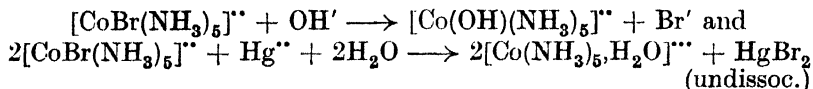
\* For recent experimental work see W. Blakey, H. McCombie, and H. A. Scarborough (*J.*, 1926, 2863; *A.*, 1927, 27), H. McCombie, H. A. Scarborough, and F. F. P. Smith (*J.*, 1927, 802; *A.*, 524), B. W. Bhide and H. E. Watson (*J.*, 1927, 2101; *A.*, 1036), and G. Muchine, R. Ginsburg, and C. Moissejeva (*Ukraine Chem. J.*, 1926, 2, 136; *A.*, 1927, 524).

<sup>57</sup> *Z. physikal. Chem.*, 1924, 113, 35; *A.*, 1925, ii, 47.

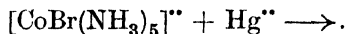




in very dilute solution. Two very good examples have been studied by J. N. Brönsted and R. Livingston,<sup>62</sup> in the reactions



Both proceed at a measurable speed at the ordinary temperature and can be followed colorimetrically; both are bimolecular, the rate of the second being determined by the process



From equations (3) and (4) it can be seen that the logarithm of the velocity coefficient plotted against the square root of the ionic strength should give a straight line of slope  $z_1 z_2$ , or  $-2$  and  $+4$ , respectively, for the two reactions. The experimental results are in excellent agreement with these predictions. Measurements on the cobaltamines are particularly appropriate, because many of them are so sparingly soluble that activity measurements by the solubility method can be made at great dilutions, and the applicability of the Debye-Hückel equation can be directly tested by an independent method.<sup>63</sup>

A. von Kiss and V. Bruckner,<sup>64</sup> studying the reaction between persulphates and the iodine ion, find Brönsted's theory confirmed in general outline with specific effects superimposed, and C. V. King<sup>65</sup> finds general agreement with the theory in the oxidation of ammonia by persulphates, catalysed by the silver ion. Numerous specific effects of various ions on the velocity of decomposition of potassium persulphate in aqueous solutions are described by A. Kailan and L. Olbrich.<sup>66</sup> H. S. Harned,<sup>67</sup> using the data of A. B. Manning<sup>68</sup> for the rate of hydrolysis of ethyl formate, assumes the rate to be given by  $k[\text{ester}]c_{\text{H}^+}$ . Manning's  $k$  varied with salt concentration: Harned makes it constant and works back to calculate  $\gamma_{\text{H}^+}\gamma_{\text{F}^-}/\gamma_{\text{HF}}$  for formic acid at different salt concentrations. The results are plausible, more so, Harned thinks, than if  $a_{\text{H}^+}$  had been used in the velocity equation. Studying the reaction between *N*-chloroacetanilide and hydrochloric acid, F. G. Soper and D. R. Pryde<sup>69</sup> conclude that the rate is best expressed by  $ka_A a_{\text{B}}$ . The values used for the activity of the chloroanilide were those pre-

<sup>62</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 435; *A.*, 319.

<sup>63</sup> J. N. Brönsted and V. K. LaMer, *ibid.*, 1924, **46**, 555; *A.*, 1924, ii, 306; V. K. LaMer, C. V. King, and C. F. Mason, *ibid.*, 1927, **49**, 363; *A.*, 314.

<sup>64</sup> *Z. physikal. Chem.*, 1927, **128**, 71; *A.*, 945.

<sup>65</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 2689.

<sup>66</sup> *Monatsh.*, 1927, **47**, 449; *A.*, 213.

<sup>67</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 1; *A.*, 206.

<sup>68</sup> *J.*, 1921, **119**, 2079.

<sup>69</sup> *J.*, 1927, 2761.

vailing in presence of the hydrochloric acid, determined by an indirect method. These varied by 13% over the hydrochloric acid concentration range (0.1—1.5*M*), whilst *k* was constant. The authors point out that if Brönsted's equation were to apply here, the activity coefficient of the intermediate complex would have to be assumed constant, which they consider unlikely in view of the variation in the coefficient of the chloroanilide itself.

Dawson and his collaborators<sup>70</sup> have shown in a series of papers that the classical mass-action equations are capable of giving a quantitative description of a great number of facts relating to the action of iodine on acetone in presence of acetic acid-sodium acetate mixtures (occasionally chloroacetic acid), and to the hydrolysis of ethyl acetate. The dissociation constants used to calculate  $p_H$  values are those based upon conductivity measurements, and these are assumed not to vary with the salt concentration. It is necessary to assume a specific catalytic action of the hydrogen ion, the acetate ion, the hydroxyl ion, and of the undissociated acetic acid. The very satisfactory results, however, will not bear very definitely on the activity problem until the work is extended to the action of "strong" acids.

The "dual" theory of acid catalysis, illustrated by Dawson's work, has lately been applied again to the hydrolysis of sucrose.<sup>71</sup> The value of *k*, the unimolecular velocity coefficient, appears, moreover, to be raised or lowered by glycerol according as the catalyst is a strong or a weak acid, but to be uniformly increased by the presence of neutral salts. A. Hantzsch and A. Weissberger<sup>71a</sup> also have dealt with the sucrose inversion and put forward a theory that water forms with strong acids complexes which ionise and are catalytically active, and with weak acids ester-like complexes which are inactive.

Soper and Pryde<sup>69</sup> point out that electrolytes may exert a considerable influence on the solubility of a non-electrolyte and therefore, according to the activity theory, should alter its rate of reaction. In this connexion we may note that J. C. Andrews and F. P. Worley<sup>72</sup> find that sodium chloride has no effect on the mutarotation of  $\alpha$ -glucose in water: this agrees with Brönsted's theory.

<sup>70</sup> H. M. Dawson and J. S. Carter, *J.*, 1926, 2282; *A.*, 1926, 1108; H. M. D. and N. C. Dean, *J.*, 1926, 2872; H. M. D. and C. R. Hoskins, *J.*, 1926, 3166; H. M. D., *J.*, 1927, 213, 458, 756, 1290; H. M. D. and W. Lowson, *J.*, 1927, 2107, 2444; *A.*, 27, 117, 214, 320, 527, 737, 1150.

<sup>71</sup> H. Colin and A. Chaudun, *J. Chim. physique*, 1926, **23**, 808; 1927, **24**, 507; *A.*, 26, 835.

<sup>71a</sup> *Z. physikal. Chem.*, 1927, **125**, 251; *A.*, 525.

<sup>72</sup> *J. Physical Chem.*, 1927, **31**, 882; *A.*, 736.

Finally, it should be mentioned that the theory attributing catalytic activity principally to the unhydrated hydrogen ion does not seem to be receiving experimental support.<sup>73</sup>

The situation might be summarised as follows. There is no theoretical reason why concentrations should simply be replaced by activities in velocity equations. Empirically, this procedure gives sometimes better and sometimes worse results, as might be expected when minor complications abound. Brönsted's equation involving the activity coefficient of an intermediate complex is not open to experimental test except in ionic reactions. Here at low concentrations it gives excellent results. (Brönsted's is essentially a concentration hypothesis although the equation involves activity coefficients.) At higher concentrations specific effects are superimposed. Numerous catalytic reactions proceed at any rate *as though* both the hydrogen ion and the undissociated acid, as well as the acid anion, had specific catalytic properties. For weak acids, even in presence of their salts, the classical equations seem to be applicable over a considerable range.

*Miscellaneous Reactions.*—Kinetic studies have been made, which cannot be adequately summarised under one heading, of a number of various reactions, including the Landolt reaction<sup>74</sup>; the decomposition and oxidation of dithionic acid<sup>75</sup>—the first stage in oxidation is hydrolysis; oxime formation<sup>76</sup>; the conversion of ammonium thiocyanate into thiourea and *vice versa*<sup>77</sup>—both unimolecular reactions; and many others.

### *Heterogeneous Reactions.*

Numerous studies made during the past year continue to show how equations based upon the adsorption theory can give an adequate description of the kinetics of surface reactions. R. E. Burk<sup>78</sup> finds the decomposition of ammonia on the surface of a heated molybdenum wire to be a reaction of zero order—complete covering of active surface—with a true heat of activation of 53,200 cal. G. M. Schwab<sup>79</sup> finds the rate of decomposition of ammonia at low pressures to be proportional to the presence of ammonia and inversely to a linear function of the pressures of nitrogen

<sup>73</sup> M. Bergstein, *Physical Chem.*, 1927, **31**, 178; **A.**, 321; G. Schmid and R. Olsen, *Z. physikal. Chem.*, 1926, **124**, 97; **A.**, 1927, 21.

<sup>74</sup> A. Skrabal and A. Zohorka, *Z. Elektrochem.*, 1927, **33**, 42; **A.**, 319.

<sup>75</sup> D. M. Yost and R. Pomeroy, *J. Amer. Chem. Soc.*, 1927, **49**, 703; **A.**, 425.

<sup>76</sup> A. Ölander, *Z. physikal. Chem.*, 1927, **129**, 1; **A.**, 1036.

<sup>77</sup> A. N. Kappanna, *J. Indian Chem. Soc.*, 1927, **4**, 217; **A.**, 943.

<sup>78</sup> *Proc. Nat. Acad. Sci.*, 1927, **13**, 67; **A.**, 426.

<sup>79</sup> *Z. physikal. Chem.*, 1927, **128**, 161; **A.**, 946.



and hydrogen. According to A. F. Benton and J. C. Elgin<sup>80</sup> the rate of reaction between hydrogen and oxygen in contact with metallic silver is proportional to the pressure of hydrogen, and independent of that of the oxygen. It is reduced by the presence of steam. The decomposition of hydrogen peroxide vapour<sup>81</sup> in contact with quartz is of zero order, and retarded by oxygen, and in contact with platinum, of the first order. The velocity of interaction of hydrogen sulphide and sulphur dioxide in Pyrex vessels varies as the pressure of sulphur dioxide and as the  $\frac{3}{2}$  power of the pressure of hydrogen sulphide.<sup>82</sup> A. F. Benton and T. L. Williams<sup>83</sup> find a much smaller rate of interaction of carbon monoxide and oxygen in contact with quartz glass than that originally found by Bodenstein and Ohlmer, and conclude that pure quartz glass is a relatively inactive catalyst. They find the rate to vary as  $[O_2][CO]^{1/2}$ . Bodenstein and Ohlmer had found inverse proportionality to carbon monoxide pressure. This illustrates the varying adsorptive properties of different kinds of quartz.

Evidence is still accumulating to show that catalytic surfaces have centres of varying activity. Direct measurements of the adsorption of carbon monoxide and of oxygen by powdered quartz glass indicate that less than 3% of the surface can be involved in the catalytic oxidation.<sup>83</sup> J. A. Almquist<sup>84</sup> estimates that only about one atom in 1000 of pure iron is active in catalysing the ammonia synthesis, and (Miss) W. M. Wright<sup>85</sup> concludes that 4–8% of the area of charcoal is effective in catalysing the oxidation of various organic acids. F. H. Constable,<sup>86</sup> from the fact that two simultaneous reactions undergone by allyl alcohol when passed over heated copper are differently influenced by changes in the physical state of the catalyst, concludes that there are two independent centres of activity for the two reactions. Similarly, G. I. Hoover and E. K. Rideal<sup>87</sup> find that the two alternative decompositions of ethyl alcohol by thoria show a specific behaviour with regard to poisons which points to the same conclusion. Burk<sup>78</sup> finds that the rate of decomposition of ammonia on molybdenum, although strongly retarded by nitrogen, does not approach zero as the surface becomes saturated with nitrogen; thus there must be

<sup>80</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 3027; *A.*, 1927, 118.

<sup>81</sup> L. W. Elder, jun., and E. K. Rideal, *Trans. Faraday Soc.*, 1927, **23**, 545; *A.*, 1035.

<sup>82</sup> H. A. Taylor and W. A. Wesley, *J. Physical Chem.*, 1927, **31**, 216; *A.*, 318.

<sup>83</sup> *Ibid.*, 1926, **30**, 1487; *A.*, 1927, 28.

<sup>84</sup> *J. Amer. Chem. Soc.*, 1926, **48**, 2820; *A.*, 1927, 29.

<sup>85</sup> *J.*, 1927, 2323; *A.*, 1039.

<sup>86</sup> *Proc. Roy. Soc.*, 1926, [A], **113**, 254; *A.*, 1927, 27.

<sup>87</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 104; *A.*, 215.

a reaction on certain parts of the surface which the nitrogen cannot poison, or else the nitrogen film itself has a certain catalytic property. The possibility that unimolecular gas films on catalysts have, in general, some specific catalytic activity should not be left out of consideration; in many examples it would provide an alternative to the hypothesis of non-uniformity of the surface—though cumulative evidence of a varied kind seems to show that this latter assumption cannot be dispensed with. It is not surprising that the study of the more complex phenomena of biochemistry leads to similar conclusions. A number of organic substances reduce methylene-blue under the influence of *Bacillus coli*, which, exposed to adverse conditions of different kinds, loses its activity not suddenly but step by step towards one after another of the substances.<sup>88</sup>

The energy relationships of heterogeneous reactions are rather complex: it is necessary to distinguish between the true and the apparent heat of activation, the latter being, in the most general case, a function of the heats of adsorption. Since this was clearly realised, a good deal of work has been done on the measurement of heats of adsorption both directly<sup>89</sup> and by indirect methods.<sup>90</sup> The general results of these show that the differential heat of adsorption is usually greatest for the first amounts adsorbed, is often of considerable magnitude, and is changed by various agencies which alter the catalytic activity. Quantitative applications to catalytic reactions are hardly possible yet.

A good deal of interesting information has been obtained about the many physical and chemical influences which cause or modify catalytic activity. A method has been proposed for finding the absolute surface of a supported metallic catalyst, based upon the determination of the electrical conductivity,<sup>91</sup> and applied to study the changes which occur when a copper catalyst is oxidised and when it is allowed to sinter. Adsorption measurements have been applied to obtain an estimate of the area of the internal surface of charcoal.<sup>92</sup> According to G. Bredig and R. Allolio,<sup>93</sup> X-ray

<sup>88</sup> J. H. Quastel and W. R. Wooldridge, *Biochem. J.*, 1927, **21**, 148, 1224.

<sup>89</sup> G. B. Kistiakowsky, E. W. Flosdorf, and H. S. Taylor, *J. Amer. Chem. Soc.*, 1927, **49**, 2200; *A.*, 1021; W. A. Dew and H. S. Taylor, *J. Physical Chem.*, 1927, **31**, 277; *A.*, 305; S. J. Gregg, *J.*, 1927, 1494; *A.*, 820; R. A. Beebe, *J. Physical Chem.*, 1926, **30**, 1538; *A.*, 1927, 23; G. B. Kistiakowsky *Proc. Nat. Acad. Sci.*, 1927, **13**, 1; *A.*, 314.

<sup>90</sup> W. G. Palmer, *Proc. Roy. Soc.*, 1927, [A], **115**, 227; *A.*, 722.

<sup>91</sup> F. H. Constable, *Nature*, 1927, **119**, 349; *A.*, 322; *J.*, 1927, 1578; *A.*, 839.

<sup>92</sup> W. E. Garner, D. McKie, and B. C. J. G. Knight, *J. Physical Chem.*, 1927, **31**, 641; *A.*, 617.

<sup>93</sup> *Z. physikal. Chem.*, 1927, **126**, 41; *A.*, 502.

examination fails to throw any light on structural differences between active and inactive catalysts. An interesting observation, related to promoter action, is that zinc oxide, mixed with copper oxide, is completely reduced by hydrogen at 300°. <sup>94</sup>

It is an important fact that in a heterogeneous catalytic reaction between two substances both must usually be adsorbed and brought under the direct influence of the catalyst. This appears to be exemplified in an interesting way by some considerations put forward by H. Remy <sup>95</sup> in discussing the catalytic combination of oxygen and hydrogen. If metals are arranged as far as possible in the order of their capacity for taking up hydrogen and oxygen respectively, it appears that those with a large affinity for hydrogen are most active when charged as far as possible with oxygen and *vice versa*.

Comparatively little work has been done on reactions actually occurring in the solid state. W. Jander <sup>96</sup> has worked out a theory of the interaction of two solids, based upon the laws of diffusion, which he finds to be confirmed experimentally. J. Hume and B. Topley <sup>97</sup> have studied the dehydration of calcium carbonate hexahydrate. The rate increases to a maximum at about 50% decomposition in accordance with the view that reaction occurs at the interface between the two solid phases. The presence of different adsorbed substances has a pronounced effect.

### *Photochemical Reactions.*

Since the last report on Photochemistry was written (1925), photochemical researches have proceeded principally along established lines, but with improving technique and an increasingly clear theoretical background. Measurements of the number of molecules transformed for each quantum of light absorbed continue to claim attention. It is now realised that there is no point in regarding individual measurements as a test of Einstein's law, which is really axiomatic as far as it goes. Such experimental evidence as it requires is to be found in the fact that it represents a limiting rule to which a majority of photochemical changes tend to conform. This approximate conformity is due to the accident that usually the primary photochemical process and the gross result of the change are very simply related. The important thing is that conspicuous deviations allow the detection of more elaborate reaction mechanisms such as chain reactions (see special section).

<sup>94</sup> W. Rogers, jun., *J. Amer. Chem. Soc.*, 1927, **49**, 1432; **A.**, 737.

<sup>95</sup> *Z. anorg. Chem.*, 1926, **157**, 329; **A.**, 1927, 28.

<sup>96</sup> *Ibid.*, 1927, **163**, 1; **166**, 31; **A.**, 736, 1037.

<sup>97</sup> *Proc. Leeds Phil. Lit. Soc. (Sci. Sec.)*, 1927, **1**, 169; **A.**, 526.

Quantum efficiencies approaching those indicated by the law of equivalence are found in the decomposition of aqueous formic acid solutions<sup>98</sup>; they vary somewhat with the wave-length, but it is interesting to note that the two alternative decompositions of formic acid occur in proportions which do not vary with the wave-length. The photodecomposition of chlorine-water has an efficiency of 1.6 to 2.0, which varies little with wave-length<sup>99</sup>; the conversion of lactic acid into acetaldehyde and carbon dioxide in presence of uranyl salts has an efficiency of about unity,<sup>1</sup> whilst the decomposition of oxalic acid solutions has a small and variable one, de-activation apparently occurring very easily.<sup>2</sup> For the photolysis of potassium nitrate solutions<sup>3</sup> the quantum efficiency is very small for wave-lengths greater than 280  $\mu$  but increases rapidly for shorter wave-lengths; at 254  $\mu$  it is a function of the hydrogen-ion concentration. Very small efficiencies have been found for two examples of the inverse process, chemiluminescence, the oxidation of phosphorus,<sup>4</sup> and of luciferin.<sup>5</sup>

Systematic studies of a number of photochemical reactions in relation to the influence of concentration, addition of foreign substances, temperature, and other factors have been made which cannot be adequately summarised here.<sup>6</sup>

The influence of intermittent light has been studied by M. Padoa and N. Vita,<sup>7</sup> who conclude from their results that molecules which absorb light in one period of illumination by a given kind of light may suffer different fates according to the nature of the light to which they are exposed in the interval.

The oxidation of hydriodic acid in presence of iodine is another example of a reaction involving a halogen where the rate is proportional to the square root of the light intensity. Thus the

<sup>98</sup> A. J. Allmand and L. Reeve, *J.*, 1926, 2852; *A.*, 1927, 29.

<sup>99</sup> A. J. Allmand, P. W. Cunliffe, and R. E. W. Maddison, *J.*, 1927, 655; *A.*, 427.

<sup>1</sup> R. H. Müller, *Biochem. Z.*, 1926, 178, 77; *A.*, 1927, 119.

<sup>2</sup> A. J. Allmand and L. Reeve, *J.*, 1926, 2834; *A.*, 1927, 29.

<sup>3</sup> D. S. Villars, *J. Amer. Chem. Soc.*, 1927, 49, 326; *A.*, 323.

<sup>4</sup> E. J. Bowen and E. G. Pells, *J.*, 1927, 1096; *A.*, 633.

<sup>5</sup> E. N. Harvey, *J. Gen. Physiol.*, 1927, 10, 875; *A.*, 901.

<sup>6</sup> A. J. Allmand and collaborators, refs. 98, 99, 2; J. L. R. Morgan and R. H. Crist, *J. Amer. Chem. Soc.*, 1927, 49, 16, 338, 960; *A.*, 216, 323, 428; D. E. Wobbe and W. A. Noyes, jun., *J. Amer. Chem. Soc.*, 1926, 48, 2856; *A.*, 1927, 30; F. Wachholtz, *Z. physikal. Chem.*, 1927, 125, 1; *A.*, 323; E. J. Bowen and C. W. Bunn, *J.*, 1927, 2353; *A.*, 1040; A. Berthoud and J. Béraneck, *Helv. Chim. Acta*, 1927, 10, 289; *A.*, 528; *J. Chim. physique*, 1927, 24, 213; *A.*, 528; A. Berthoud and G. Nicolet, *Helv. Chim. Acta*, 1927, 10 417; *A.*, 739.

<sup>7</sup> *Gazzetta*, 1927, 57, 187; *A.*, 528.

primary process seems to be the dissociation of the iodine molecules to give atoms which catalyse the oxidation.<sup>8</sup>

Recently R. G. W. Norrish<sup>9</sup> has shown that in illuminated nitrogen peroxide an equilibrium  $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$  is set up, and suggests that in the photocatalytic decomposition of nitrogen pentoxide the  $\text{NO}_2$  first gives NO which then reacts with  $\text{N}_2\text{O}_5$  to give  $3\text{NO}_2$ .

Several new investigations on the sensitising actions of mercury vapour in photochemical changes have been made. Excited mercury atoms appear to be able to cause the disruption of the linkings C-H, N-H, and O-H in such compounds as the alcohols, ammonia, and so on.<sup>10</sup> A. L. Marshall<sup>11</sup> has studied the synthesis of formaldehyde from carbon monoxide and hydrogen, and concludes that atomic hydrogen is first produced, since the rate depends upon the square root of the hydrogen pressure. R. G. Dickinson and A. C. G. Mitchell<sup>12</sup> have also studied the decomposition of ammonia under similar conditions.

If a quantum  $h\nu$  is given to a diatomic molecule which requires energy  $D$  to decompose it, the excess,  $(h\nu - D)$ , should appear as translational energy. T. R. Hogness and J. Franck<sup>13</sup> have shown that when sodium iodide vapour at  $650^\circ$  is decomposed by ultra-violet light of shorter wave-length than the critical value, the Doppler effect of the light emitted by the sodium increases with the frequency of the activating light in accordance with theoretical expectations.

The relation between photochemistry and the phenomena of fluorescence is a close one.<sup>14</sup> In this connexion, it is of interest to note that E. Gaviola has devised a method for measuring the duration of fluorescence,<sup>15</sup> and that measurements<sup>16</sup> on various substances give values for the duration of the order  $5 \times 10^{-9}$  second.

The combination of hydrogen and chlorine is still, after more than half a century, a plentiful source of problems. The active frequencies appear not to be confined to any restricted regions,

<sup>8</sup> A. Berthoud and G. Nicolet, *Helv. Chim. Acta*, 1927, **10**, 475; **A.**, 736.

<sup>9</sup> *J.*, 1927, 761; **A.**, 528.

<sup>10</sup> H. S. Taylor and J. R. Bates, *Proc. Nat. Acad. Sci.*, 1926, **12**, 714; **A.**, 1927, 217. Compare also H. S. Taylor, *J. Amer. Chem. Soc.*, 1926, **48**, 2840; **A.**, 1927, 30.

<sup>11</sup> *J. Physical Chem.*, 1926, **30**, 1634; **A.**, 1927, 216.

<sup>12</sup> *Proc. Nat. Acad. Sci.*, 1926, **12**, 692; **A.**, 1927, 217.

<sup>13</sup> *Z. Physik*, 1927, **44**, 26; **A.**, 947.

<sup>14</sup> J. Perrin, *Compt. rend.*, 1927, **184**, 1097; **A.**, 609; F. Perrin, *ibid.*, p. 1121; **A.**, 609.

<sup>15</sup> *Z. Physik*, 1927, **42**, 853; **A.**, 712.

<sup>16</sup> E. Gaviola, *ibid.*, p. 862; **A.**, 712; E. Gaviola and P. Pringsheim, *ibid.*, 1927, **43**, 384; **A.**, 810.

since, when light is filtered through chlorine, its photochemical activity falls rapidly, not towards zero, but towards a definite residual value. Thus some of the very feebly absorbed frequencies must be active.<sup>17</sup> G. B. Kistiakowsky<sup>18</sup> states that intensive drying of chlorine does not affect the absorption; nor is any appreciable part of the absorbed light re-emitted by fluorescence. Thus it seems hard to believe that water can play any part in the dissociation of chlorine molecules. Therefore in the hydrogen-chlorine reaction water must play a part at some other stage.

There has always been some disagreement about the form of the equations for the rate of reaction. N. Thon<sup>19</sup> now questions Chapman's result that excess of hydrogen has a slight retarding effect; in a critical survey of the whole problem, he suggests<sup>20</sup> the general formula  $\frac{dx}{dt} = \frac{k[\text{Cl}_2]^2[\text{H}_2]}{k'[\text{H}_2][\text{O}_2] + k''[\text{Cl}_2]}$  and shows that, on the whole, the apparently divergent results of different investigators can be regarded as special cases of this general equation. With regard to the inhibition by oxygen, he calculates<sup>21</sup> that the amount of water formed under ordinary conditions is negligible in comparison with the hydrogen chloride produced.

E. Cremer<sup>22</sup> suggests the reaction scheme: (1)  $\text{Cl}_2 + \text{light} = \text{Cl}^a + \text{Cl}$ ; (2)  $\text{Cl}^a + \text{Cl}_2 = \text{Cl}_3^a$ ; (3)  $\text{Cl}_3^a + \text{H}_2 = 2\text{HCl} + \text{Cl}^a$ ; (4)  $\text{Cl}^a + \text{O}_2 = \text{O}_2^a + \text{Cl}$ ; (5)  $\text{Cl}_3^a + \text{O}_2 = \text{O}_2^a + \text{Cl}_2 + \text{Cl}$ ; (6)  $\text{Cl}_3^a = \text{Cl}_2 + \text{Cl}$ ; (7)  $\text{Cl}^a = \text{Cl}$ .

The possible intervention of water vapour is not taken into account. In this mechanism the oxygen no longer acts as a remover of atomic hydrogen—a rôle which the smallness of the water formation makes improbable—but degrades the energy of the chlorine as in the original theory of Chapman. Certain discrepancies between the results of various investigators are explained by the suggestion that reaction (6) may be catalysed by the walls of the reaction vessel. Possibilities of this kind certainly ought to be taken into account.

This Mona Lisa of chemical reactions still smiles its bewitching smile, leaving us in doubt whether even yet the secret has been completely fathomed.

C. N. HINSHELWOOD.

<sup>17</sup> W. Taylor, *Trans. Faraday Soc.*, 1927, **23**, 31; *A.*, 216; W. Taylor and A. Elliot, *ibid.*, pp. 38, 583; *A.*, 216, 1039.

<sup>18</sup> *J. Amer. Chem. Soc.*, 1927, **49**, 2194; *A.*, 1040.

<sup>19</sup> *Z. physikal. Chem.*, 1926, **124**, 327; *A.*, 1927, 323.

<sup>20</sup> "Die Chlorknallgasreaktion," *Fortschritte der Chemie, Physik und physikalische Chemie*, Band 18, Heft 11 (Berlin, 1926).

<sup>21</sup> *Op. cit.*, p. 21.

<sup>22</sup> *Z. physikal. Chem.*, 1927, **128**, 285; *A.*, 947.



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